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Reactions of Dianionic Carbonylmetalates with Heteroallenes: Reduction of Carbonylsulfide, Thioisocyanates, Isocyanates and Carbodiimides by Group 6 and 8 Carbonylmetalates

by

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Abstract. Dianionic carbonylmetalates of the group 6 and group 8 metals can reduce a number of heteroallenes X=C=Y to coordinated C X ligands, provided X is a first row element (N or O) which can form a strong triple bond with C. Thus $Na_2[M(CO)_4]$ (M = Fe, Ru) and $Na_2[M(CO)_5]$ (M = Cr,W) react readily with COS to give $[M(CO)_5]$ (M = Fe, Ru) and $[M(CO)_6]$ (M = Cr,W) in good yield, as established by absorbance mode IR for Fe and W and by isolation of the known derivatives $[M(CO)_4I_2]$ (M = Fe, Ru) and $[N(n-Bu)_4][M(CO)_5Br]$ (M = Cr, W), while CS_2 does not give thiocarbonyl complexes with $Na_2[W(CO)_5]$ or $Na_2[Fe(CO)_4]$. It is suggested on the basis of IR and stoichiometry that the COS reductions are reductive disproportionations leading to thiocarbonate formation. Thioisocyanates RNCS (R = Ph, Me) give moderate yields of the corresponding isonitrile complexes $[M(CO)_4(CNR)]$ with $Na_2[Fe(CO)4]$, but not with $Na_2[Ru(CO)4]$. A similar reaction of PhNCS with $Na_2[Cr(CO)_5]$ gives low yields of $[Cr(CO)_5(CNPh)]$, but $[W(CO)_5(CNPh)]$ can only be isolated after addition of oxalylchloride to the intermediate thioisocyanate complex. Reduction of PhNCO with $Na_2[W(CO)_5]$ leads to 84% and 5% solution yields of $[W(CO)_6]$ and $[W(CO)_5(CNPh)]$, consistent with control of the reduction of unsymmetrical heteroallenes by the relative triple bond strengths in the product C≡X ligands ($C≡O > C≡N > C≡S$).
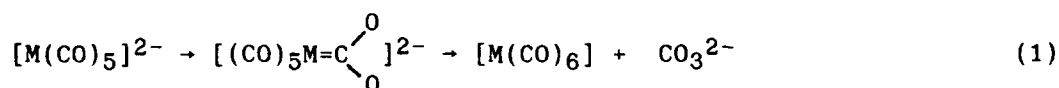
transition metals,
Carbonyls,
Iron,
Rubidenium.

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We have previously reported that dianionic carbonylmetalates charac-
teristically induce reductive disproportionation of carbon dioxide to
coordinated carbon monoxide and carbonate,[3] and we also established, in the case
of the pentacarbonyl dianions of the group 6 metals, that these reactions
proceeded through intermediate η^1-CO_2 complexes (Eq. 1).[3] We suggested that the
facility of these reactions reflected the enhanced nucleophilicity of the CO_2
oxygen atoms as a result of the transfer of electron density from the transition
metal center onto the oxygen atoms of the coordinated CO_2, and it is not
unreasonable that η^1-coordination of other heteroallenes[4] to dianionic carbonyl
metallates could result in similar activation of the heteroatoms and lead to
reductive disproportionation, particularly since the reactions of heteroallenes
with some neutral electron-rich transition metal complexes have been reported to
result in examples of the general reductive disproportionation reaction shown in
Eq. 2.

$$[M(CO)_5]^{2-} \rightarrow [(CO)_5M=C{\overset{O}{\underset{O}{\diagup}}}]^{2-} \rightarrow [M(CO)_6] + CO_3^{2-} \tag{1}$$

$$2e^- + 2X=C=Y \rightarrow X\equiv C + CXY_2^{2-} \tag{2}$$

Heteroallene reductive disproportionation is probably best established for
thioisocyanates (RN=C=S), particularly with platinum group metals, several of
which have been reported to give complexes containing both isonitrile and di-
thiocarbonimidato ($S_2C=NR$) ligands following treatment with thioisocyanates.[5,6,7]
It has also been reported that carbon disulfide undergoes reductive dispro-
portionation with Rh(I) complexes[8] and that carbonyl sulfide undergoes reductive
disproportionation with $[V(\eta\text{-}C_5H_5)_2]$[9] and with zero valent complexes of the
iron[10] and nickel[11] triads. Urylene (NR(O)C=NR) complexes have been formed from
isocyanates (RN=C=O),[12,13,14,15] and there are two systems in which a reaction

1

with a carbodiimide leads to products indicative of reductive dis-
proportionation.[16,17]

The possibility that they might promote facile reductive disproportionation
has led us to examine the reactions of dianionic carbonylmetalates of the group
6 and 8 metals with a range of heteroallenes, with the objective of gaining a
better general understanding of heteroallene disproportion by determining its
facility with a variety of substrates and by determining the preferred direction
of reduction of unsymmetrical heteroallenes such as isocyanates and
thioisocyanates.

Previous studies of the reactions of heteroallenes other than CO_2 with
dianionic transition metal complexes are limited. Fehlhammer has reported that
$Na_2[Cr(CO)_5]$ reacts with CS_2 in the presence of $[Pt(PPh_3)_2Cl_2]$ to give a
trithiocarbonate bridged binuclear complex $[(CO)_5Cr(\mu-SCS_2)Pt(PPh_3)_2]$ in
moderate yield,[18] and more recently that sulfide can be abstracted by phosgene
from the intermediate 1:1 adduct of PhNCS with $[Cr(CO)_5]^{2-}$ to give the
isonitrile complex $[Cr(CO)_5(CNPh)]$.[19] Similar reactions of the chromium
pentacarbonyl dianion with carbodiimides RN=C=NR (R = C_6H_{11}, Ph) have been
reported to give 1:1 adducts which could also be converted to isonitrile
complexes by treatment with phosgene or to diaminocarbenes by addition of
HCl.[20,21]

Experimental Section

General, Solvents and Reagents. All manipulations were conducted under prepurified dinitrogen or argon by means of standard Schlenk techniques unless otherwise indicated. Tetrahydrofuran (THF) and diethyl ether were predried over sodium wire and distilled under N_2 from sodium benzophenone ketyl. Toluene was dried over sodium wire and distilled under N_2 from powdered CaH_2. n-Pentane was stirred over concentrated H_2SO_4 for 24 hours, neutralized over anhydrous K_2CO_3 for 12 hours, and distilled under N_2 from $Li[AlH_4]$. Dichloromethane was distilled from powdered CaH_2. All solvents wre degassed immediately before use.

The following commercial reagents were used as received: $[Cr(CO)_6]$ (Pressure), $[W(CO)_6]$ (Pressure), NMe_3 (Matheson), $[Ru_3(CO)_{12}]$ (Strem), naphthalene (MCB or Baker), I_2 (Mallinckrodt), $[NBu_4]Br$ (Alfa), $Me_3N \cdot 2H_2O$ (Aldrich), oxalylchloride (Fluka), PhNCS (Alfa), PhNCO (Aldrich), and MeNCO (Aldrich). Sodium (Fisher) and potassium (Baker) were freshly cut under N_2, and lithium metal, alloyed with 1% sodium (Alfa-Ventron or Cerac), was freshly cut under sodium dried mineral oil and handled under argon. Liquid NH_3 was freshly distilled from sodium before use. CS_2 (Fisher) was dried over 3Å molecular sieves, and COS was passed through a 40 cm column packed with a 1:1 mixture of anhydrous $CaCl_2$ and activated 3Å molecular sieves (Linde). CH_3NCS (Aldrich) was distilled from P_2S_5 and PhNCNPh ws prepared according to the literature.[22] Collman's reagent ($Na_2[Fe(CO)_4] \cdot 1.5$p-dioxane, 99.5%), was purchased from Ventron-Alfa and rinsed with THF immediately before use to remove trace quantities of $Na[HFe(CO)_4]$. Solutions of alkali metal salts of the pentacarbonyl dianions of the group 6 metals ($M'_2[M(CO)_5]$) were prepared in THF by naphthalenide reduction of the corresponding amine complexes $[M(CO)_5(NMe_3)]$ as previously reported.[23] $Na_2[Ru(CO)_4]$ was prepared by Na reduction of $[Ru_3(CO)_{12}]$ in NH_3, as reported in the literature.[24]

3

Infrared spectra were recorded on Perkin-Elmer model 457A or model 683 spectrophotometers. Solution samples were analyzed in gas-tight demountable NaCl cells (0.1 mm pathlength) sealed with 5 mm rubber serum caps. Nujol mulls were analyzed as thin films between NaCl plates. Spectra were calibrated relative to the sharp 1601 cm^{-1} band of polystyrene. Mass spectra were recorded on an AEI Ms-9 double-focusing spectrometer.

Reaction of $Na_2[Fe(CO)_4] \cdot 1.5p$-dioxane with Excess COS and Conversion of the Product $[Fe(CO)_5]$ to cis-$[Fe(CO)_4I_2]$. Dried COS (50.0 mL, xg, 2.07 mmol) was syringed over 1 min into a vigorously stirred tan suspension of $Na_2[Fe(CO)_4] \cdot$-1.5p-dioxane (0.322 g, 0.93 mmol) in 26.0 mL THF at ambient temperature. After 10 min the reaction mixture was allowed to settle and the principal ν_{CO} absorptions in IR spectra of the pale yellow solution were those of $[Fe(CO)_5]$ at 2023 m^{-1} (s) and 1992(x) cm^{-1}. Absorbance mode spectra indicated an effective $[Fe(CO)_5]$ concentration of 0.026 $\underline{M}$ (based on $\epsilon = 3500$ M^{-1} cm^{-1} for the 1992 cm^{-1} band), corresponding to a 73% yield. The solution was filtered into a vessel containing I_2 (0.230 g, 0.91 mmol). The solution changed to a deep red-brown color with gas evolution. Solution IR spectra after 12 min showed quantitative consumption of $[Fe(CO)_5]$ and the appearance of ν_{CO} absorptions consistent with formation of cis-$[Fe(CO)_4I_2]$.[25] Solvent was removed under reduced pressure, and the microcrystalline red-black product was maintained at 0.05 mm Hg for 2 hours. Extraction with 20 mL of toluene, filtration and solvent removal in vacuo provided microcrystalline red-black cis-$[Fe(CO)_4I_2]$ (0.281 g, 0.67 mmol ≈ 72% relative to $Na_2[Fe(CO)_4] \cdot 1.5p$-dioxane). IR (toluene): 2138 (m), 2092 (s), 2072 (m) cm^{-1}. The initial THF-insoluble solid was dried under reduced pressure to yield a tan powder (0.091 g).

Reaction of $Na_2[Ru(CO)_4]$ with Excess COS and Conversion of the Product
$[Ru(CO)_5]$ to $\underline{cis}$-$[Ru(CO)_4I_2]$. Dried COS (50.0 mL,xg, 2.10 mmol) was syringed

in the dark into a rapidly stirred yellow-tan suspension of $Na_2[Ru(CO)_4]$ (0.238

g, 0.92 mmol) in 30 mL THF at 4°C over 1 min. After 10 min. the flocculent pale

yellow precipitate was permitted to settle. Solution IR spectra showed the

appearance of strong ν_{CO} absorptions at 2045 and 1994 cm^{-1} consistent with the

presence of $[Ru(CO)_5]$.[25] The THF solution was filtered into a vessel containing

I_2 (0.223 g, 0.88 mmol) at 4°C. After 30 min at 4°C and 25 min. at R.T., the

stirred mixture gave a clear light orange solution. Solution IR spectra

contained ν_{CO} absorptions consistent with formation of $\underline{cis}$-$[Ru(CO)_4I_2]$.[26]

Removal of solvent under reduced pressure gave a dark orange-red residue from

which excess I_2 was sublimed (60°C, 0.05 mm Hg) over 2 hours, to leave a bright

orange-yellow solid. Extraction with 30 mL 2:1 CH_2Cl_2:THF, filtration, and

solvent removal $\underline{in}$ $\underline{vacuo}$ yielded powdery golden yellow $\underline{cis}$-$[Ru(CO)_4I_2]$ (0.307 g,

0.66 mmol ▪ 72% based on $Na_2[Ru(CO)_4]$). IR (CH_2Cl_2): 2171 (m), 2118 (s), 2080

cm^{-1} (m), 2056 (x) cm^{-1}. The original THF-insoluble residue was dried under

reduced pressure to give 0.108 g of orange-brown solid. Nujol mull IR spectra

of this were dominated by broad absorptions at 1450-1400 and ca. 900 cm^{-1}.

Reaction of $Na_2[Cr(CO)_5]$ with Excess COS and Conversion of the Product
$[Cr(CO)_6]$ to $[N(n-Bu)_4][Cr(CO)_5Br]$. Dried COS (55 mL, 0.136 g, 2.26 mmol) was

syringed into a 0.044 $\underline{M}$ solution of $Na_2[Cr(CO)_5]$ in THF (23.6 mL, 1.04 mmol) at

-78°C over 1 min. The mixture immediately bleached, then gave a milky yellow

suspension which precipitated as the mixture was warmed to R.T. IR spectra of

the filtered solution indicated quantitative consumption of $Na_2[Cr(CO)_5]$ and the

formation of $[Cr(CO)_6]$ (ν_{CO} 1978 (s) cm^{-1}). Weaker bands were also observed at

1920 (m) and 1870 (sh) cm^{-1}, consistent with the presence of some

$Na[Cr(CO)_5SC(O)H]$.[27] The precipitate was washed with 2 x 5 mL THF. Solid

[N(n-Bu)$_4$]Br (0.335 g, 1.04 mmol) and Me$_3$NO·2H$_2$O (0.115 g, 1.04 mmol) were added sequentially to the stirred filtrate. The added solid dissolved within 3.5 hours. IR spectra of the golden-yellow filtered solution indicated complete consumption of [Cr(CO)$_6$]. After solvent removal _in vacuo_ the product was rinsed with 4 x 20 mL of n-pentane and dried under reduced pressure to give [N(n-Bu)$_4$]-[Cr(CO)$_5$Br][28] as a powdery mustard-yellow solid (0.435 g, 0.85 mmol ≡ 82% relative to [Cr(CO)$_5$(NMe$_3$)]). IR (THF): 2059 (w), 1963 (sh), 1918 (vs), 1860 (ms) cm^{-1}. The original THF-insoluble precipitate was dried _in vacuo_ over 20 min to provide 0.12 g of greenish-tan solid.

Reaction of Na$_2$[W(CO)$_5$] with Excess COS and Conversion of the Product [W(CO)$_6$] to [N(n-Bu)$_4$][W(CO)$_5$Br]. Gaseous COS (40.0 mL, 0.099 g, 1.65 mmol) was syringed into a vigorously stirred 0.020 M solution of Na$_2$[W(CO)$_5$] in THF (39.0 mL, 0.78 mmol) at -78°C over 2 min. The reaction mixture rapidly bleached to a clear light yellow, then clouded. The suspension was warmed to R.T., and dry N$_2$ was briefly (2 min) bubbled through the mixture (this facilitated precipitation of a flocculent pale yellow solid). THF (35 mL) was added, and the precipitate was permitted to settle. IR spectra of the clear, light yellow filtered solution indicated complete consumption of Na$_2$[W(CO)$_5$] and the formation of [W(CO)$_6$]. Weaker bands at 1910 (m) and 1858 (w) cm^{-1} were also observed, consistent with the presence of some Na[W(CO)$_5$SC(O)H].[29] Absorbance mode IR spectra of a 1.0 mL aliquot of the supernatant indicated an 8.02 M concentration of [W(CO)$_6$] (based on ϵ = 14,400 M^{-1} cm^{-1} for the 1973 cm^{-1} band), corresponding to a [W(CO)$_6$] yield of 0.59 mmol, or 74% relative to [W(CO)$_5$(NMe$_3$)]. 100 mL of H$_2$O were added to the filtered solution, and the yellow emulsion separated by addition of 40 mL of Et$_2$O and 0.50 g of NaCl. The pale yellow organic phase was decanted onto 2.50 g of anhydrous CaCl$_2$, and the aqueous phase extracted with a further 4 x 10 mL Et$_2$O. After 25 min the solution was filtered and

[N(n-Bu)$_4$]Br (0.187 g, 0.58 mmol) and Me$_3$NO·2H$_2$O (0.064 g, 0.58 mmol) were added sequentially. After 21.5 hours at room temperature the stirred solution was a clear golden yellow. Solvent removal under reduced pressure followed by 3 x 35 mL rinses with 1:1 Et$_2$O/pentane afforded an amorphous yellow ochre solid. Extraction into 20 mL of CH$_2$Cl$_2$, filtration, and solvent removal in vacuo provided flaky yellow [N(n-Bu)$_4$][W(CO)$_5$Br][30] (0.292 g, 0.45 mmol ≈ 57% relative to [W(CO)$_5$NMe$_3$]). IR (CH$_2$Cl$_2$): 2070 (w), 1964 (sh), 1918 (vs), 1847 (m) cm^{-1}. The original THF-insoluble precipitate was dried under reduced pressure to give 0.075 g of powdery buff solid. IR (Nujol): ca. 1440 (ms, vbr), 1264 (m), 904 (x) cm^{-1}.

The initially formed [W(CO)$_6$] was isolated from a similar experiment in which dry COS was added at 200 mL/min to a rapidly stirred 0.062 $\underline{M}$ solution of Na$_2$[W(CO)$_5$] (21.3 mL, 1.32 mmol) at -78°C for 30 sec. The reaction mixture immediately bleached to pale yellow, and was stirred for a further 5 min. After the mixture had settled for 25 min, the finely divided, yellow-white precipitate collected by filtration at -78°C. The wet solid was washed with H$_2$O (4 x 5 mL) at room temperature, and then with 5 mL of Et$_2$O at -60°C then dried under a slow stream of air. This gave bright white [W(CO)$_6$] (0.282 g, 0.80 mmol ≈ 61% relative to [W(CO)$_5$(NMe$_3$)]). IR (Nujol): 1980 cm^{-1}.

Reaction of Na$_2$[Fe(CO)$_4$]·1.5p-dioxane with PhNCS and Isolation of [Fe(CO)$_4$(CNC$_6$H$_5$)]. Neat PhNCS (0.77 mL, 0.87 g, 6.41 mmol) was injected into a rapidly stirred suspension of Na$_2$[Fe(CO)$_4$]·1.5p-dioxane (1.108 g, 3.20 mmol) in 20 mL THF at 4°C. The initial golden amber suspension gradually darkened to an opaque dark red color over 1 hour. After the mixture was permitted to settle, IR spectra of the deep red supernant contained the following absorptions; 2174 (s), 2063 (vs), 1993 (vs), 1966 (vs), 1922 (sh), 1878 (sh), 1593 (ms), and 1564 (m) cm^{-1}. Stirring was resumed for 20 min followed by the removal of solvent

7

under reduced pressure. The red-brown residue was extracted with 3 x 30 mL of n-pentane and the pale yellow extracts were filtered. Concentration of the filtrate to ca. 10 mL under reduced pressure followed by slow cooling to -70°C afforded feathery chiffon-yellow crystals. The pale yellow mother liquor was decanted and the crystalline solid was dried under reduced pressure to give 0.364 g of pastel yellow $[Fe(CO)_4(CNC_6H_5)]$.[31] (1.34 mmol, 41.5% relative to Collman's reagent). IR (n-pentane): 2163 (m), 2063 (s), 1998 (s), 1972 (vs), 1937 (w) cm^{-1}. MS: Parent ion at m/e = 271.

Reaction of $Na_2[Fe(CO)_4]\cdot1.5p$-dioxane with CH_3NCS and Isolation of $[Fe(CO)_4(CNCH_3)]$. A 6.88 $\underline{M}$ solution of CH_3NCS in THF (0.77 mL, 5.3 mmol) was syringed into a stirred suspension of $Na_2[Fe(CO)_4]\cdot1.5p$-dioxane (0.917 g, 2.65 mmol) in 20 mL of THF at 4°C in the absence of light. The reaction mixture gradually darkened over 2.5 hours to give a ruddy orange suspension, which was then permitted to settle. IR spectra of the supernatant contained the following absorptions: 2223 (m), 2070 (s), 1987 (s), 1961 (vs), 1925 (m), 1878 (ms, dist), 1774 (mw, br), 1588 (mw), and 1560 (x) cm^{-1}. The mixture was stirred for an additional 30 min, then stripped of solvent under reduced pressure below 0°C. Extraction with 3 x 30 mL of n-pentane at 0°C followed by concentration of the filtrate to ca. 10 mL under reduced pressure and slow cooling to -70°C provided clear yellow-white crystalline plates. After the mother liquor had been decanted, the solid was briefly dried $\underline{in}$ $\underline{vacuo}$ to yield 0.134 g of $[Fe(CO)_4(CNCH_3)]$[31] (0.64 mmol, 24.2% relative to Collman's reagent). IR (n-pentane): 2210 (s), 2071 (s), 1997 (s), 1970 (s), 1935 (m) cm^{-1}. MS: Parent ion at m/e = 209.

8

Reaction of Li$_2$[Cr(CO)$_5$] with PhNCS and Isolation of [Cr(CO)$_5$(CNC$_6$H$_5$)].
Colorless PhNCS (0.19 mL, 0.21 g, 1.59 mmol), was syringed into a stirred 0.038
$\underline{M}$ solution of Li$_2$[Cr(CO)$_5$] in THF (21.3 mL, 0.81 mmol) at -78°C. The
homogeneous deep red solution was stirred for 5 min, then warmed to R.T..
Solution IR spectra showed ν_{CO} absorptions at 2154 (mw), 2072 (m), 1988 (sh),
1960 (s), 1922 (m), 1886 (s), and 1797 (m, dist), cm^{-1}. After 48 hours, IR
spectra showed that the bands at 2153, 2070, and 1958 cm^{-1} had intensified at
the expense of the ν_{CO} absorptions at lower frequency. Solvent was removed
under reduced pressure and the residue was extracted with 3 x 25 mL of
n-pentane. The filtered solution was evaporated under reduced pressure to give
0.225 g of semicrystalline yellow-white solid. Naphthalene was sublimed away
from the crude product mixture at R.T. (0.02 torr, 1.5 hours), then at 35°C (30
min). Powdery white [Cr(CO)$_5$(CNC$_6$H$_5$)][32] was isolated by sublimation (0.02
torr, 60-95°C, 1 hour) onto a liquid nitrogen-cooled cold finger (0.033 g, 0.11
mmol, 13.9% relative to [Cr(CO)$_5$(NMe$_3$)]). IR (n-pentane): 2138 (w), 2057 (mw),
1963 (s) cm^{-1}. MS: Parent ion at m/e = 295.

**Reaction of Li$_2$[W(CO)$_5$] with MeNCS and Spectroscopic Observation of
[W(CO)$_5$(CNCH$_3$)].** Neat liquid MeNCS (0.22 mL, 0.24 g, 3.22 mmol) was syringed
into a vigorously stirred 0.024 $\underline{M}$ solution of Li$_2$[W(CO)$_5$] in THF (22.3 mL, 0.54
mmol) at -78°C. When warmed to R.T., the homogeneous golden amber mixture
darkened to a clear orange. Solution IR spectra showed quantitative consumption
of starting material and the appearance of ν_{CO} absorptions at 2200 (m), 2120
(m), 2077 (m), 1984 (sh), 1943 (vs) and 1866 (w) cm^{-1}. Solvent was removed
under reduced pressure and the orange-brown residue was extracted with 3 x 10
mL n-pentane. The faintly yellow extracts were filtered and solvent was again
evaporated under reduced pressure to give 0.349 g of pale yellow powder.
Solution IR and mass spectra indicated the presence of [W(CO)$_5$(CNCH$_3$)][33] as the

9

only detectable metal carbonyl product in this sample. IR (n-pentane): 2183 (w), 2079 (mw), 1956 (vs), 1923 (vw) cm^{-1}. MS: Parent ion at m/e = 365.

Preparation of [W(CO)$_5$(CNC$_6$H$_5$)] by Sequential Reaction of Na$_2$[W(CO)$_5$] with PhNCS and Oxalyl Chloride. Clear, colorless PhNCS (57 μl, 0.064 g, 0.47 mmol) was injected into a stirred 0.026 M solution of Na$_2$[W(CO)$_5$] in THF (20 mL, 0.52 mmol) at -78°C. IR spectra of the resultant deep burgundy red solution showed quantitative consumption of the monomeric dianion and the appearance of ν_{CO} absorptions at 2063 (vw), 1986 (mw), 1918 (m), 1875 (s), 1755 (m), 1510 (m) cm^{-1}. Oxalyl chloride (42 μl, 0.061 g, 0.48 mmol) was injected into the stirred solution, which darkened to an opaque red-brown color. After 5 min solution IR spectra exhibited absorptions at 2148 (w), 2064 (mw), 2010 (sh), 1970 (sh), 1950 (sh), 1927 (s), and 1886 (sh) cm^{-1}. The mixture was warmed to R.T., the solvent was removed under reduced pressure and the red-brown residue was extracted with 3 x 25 mL n-pentane. IR spectra of the filtered extracts indicated the presence of trace [W(CO)$_6$] (1986 cm^{-1}), together with a major species exhibiting ν_{CO} absorption at 2141 (w), 2061 (m), 1962 (s), and 1930 (w) cm^{-1}. Evaporation of solvent under reduced pressure provides a pale buff-colored powder, from which naphthalene and [W(CO)$_6$] were sublimed (0.02 torr, 40°C, 1 hour). Extraction of the pale tan residue with 10 mL of n-pentane followed by removal of solvent from the filtrate under reduced pressure afforded powdery cream-colored [W(CO)$_5$(CNC$_6$H$_5$)][32] (0.012 g, 0.03 mmol, 5.9% relative to [W(CO)$_5$(NMe$_3$)]). IR (n-pentane): 2141 (vw), 2060 (mw), 1962 (vs) cm^{-1}; (THF): 2148 (w), 2064 (mw), 1953 (ms) cm^{-1}. MS: Parent ion at m/e = 427.

Reaction of $Na_2[W(CO)_5]$ with PhNCO and Spectroscopic Quantification of the Product $[W(CO)_6]$ and $[W(CO)_5(CNC_6H_5)]$. Injection of PhNCO (0.23 mL, 0.252 g, 2.11 mmol) into a stirred 0.021 $\underline{M}$ solution of $Na_2[W(CO)_5]$ in THF (25.1 mL, 0.53 mmol) at $-78°C$ produced a pale yellow suspension containing fine white filaments. After 5 min, the reaction mixture was warmed to R.T. IR spectra of the homogeneous yellow solution indicated quantitative consumption of $Na_2[W(CO)_5]$ and formation of $[W(CO)_6]$ ($\nu_{CO} = 1973$ cm^{-1}) together with weaker bands at 2064 (sh), 2055 (vw), 1907 (m), 1712 (m), 1690 (mw, br), and 1580 (m, br) cm^{-1}. When a second portion of PhNCO (0.111 mL, 0.121 g, 1.01 mmol) was added IR spectra showed the intensification of absorptions at 2145, 2064, 1973 and 1712 cm^{-1}, and diminution of the 1907 cm^{-1} band. The two highest frequency absorptions are superimposable upon those of $[W(CO)_5(CNC_6H_5)]$ in THF, and absorbance mode IR spectra (assuming $\epsilon = 2,400$ $\underline{M}^{-1}$cm^{-1} for the 2064 cm^{-1} band) were used to calculate a $[W(CO)_5(CNC_6H_5)]$ concentration of 0.96 mM (4.5% yield relative to $[W(CO)_5(NMe_3)]$). A 1.0 mL aliquot was diluted to 3.0 mL with THF, and absorption spectra (assuming $\epsilon = 14,400$ $\underline{M}^{-1}$cm^{-1} for the 1973 cm^{-1} band) were used to calculate a $[W(CO)_6]$ concentration of 5.87 $\underline{mM}$. This was extrapolated to 17.6 $\underline{mM}$ in the original mixture (83.4% yield relative to $[W(CO)_5(NMe_3)]$).

Reaction of $Na_2[Fe(CO)_4] \cdot 1.5p$-dioxane with PhNCNPh and Isolation of $[Fe(CO)_4(CNC_6H_5)]$. Neat diphenyl carbodiimide (0.58 mL, 0.632 g, 3.25 mmol) was injected into a stirred suspension of $Na_2[Fe(CO)_4] \cdot 1.5p$-dioxane (0.558 g, 1.61 mmol) in 20 mL of THF at ambient temperature. The mixture was refluxed gently for 20 min, and the deep red-brown suspension was permitted to cool and settle. IR spectra of the supernatant showed absorptions at 2164 (mw), 2103 (w), 2060 (s), 2010 (sh), 1986 (sh), 1964 (s), 1918 (s), 1898 (s), 1879 (s), 1660 (ms),

and 1592 (s) cm^{-1}. Solvent was removed under reduced pressure and the red-brown residue was extracted with 2 x 20 mL of toluene. IR spectra of the filtered extracts indicated the presence of $[Fe(CO)_4(CNC_6H_5)]$ (2162 (mw), 2059 (s), 1993 (m), and 1963 (s) cm^{-1}, and contained weaker bands at 2105 (w) and 1663 (mw) cm^{-1}. Solvent was evaporated under reduced pressure at 40°C and the residue was extracted with 3 x 20 mL n-pentane. Removal of pentane from the filtered extracts under vacuum provided pale yellow prismatic crystals of $[Fe(CO)_4(CNC_6H_5)]$[31] (0.042 g, 0.15 mmol, 9.6% relative to Collman's reagent). IR (n-pentane): see above.

Results and Discussion

We were particularly intrigued by the possibility that reductive disproportionation of heteroallenes by dianionic carbonylmetalates could provide direct, convenient syntheses of mono-thiocarbonyl and mono-isonitrile complexes, and our experiments therefore focused on heteroallenes which might be reduced to thiocarbonyl or isonitrile ligands. These include carbon disul!.ide, carbonyl sulfide, thioisocyanates, isocyanates, and carbodiimides, and Table I summarizes the results of reactions with these substrates which gave rise to characterized organometallic products.

Reactions of Carbon Disulfide with Dianionic Carbonylmetalates. We have previously reported that CS_2 forms a 1:1 adduct with $M_2[W(CO)_5]$ (M = Li or Na),[3] and we have confirmed that excess dry CS_2 shows no tendency to abstract a S^{2-} ion from these adducts in THF over 24 hr at room temperature, as indicated by the failure to see IR absorptions corresponding to those of $[W(CO)_5(CS)]$,[34] although there was some deterioration of the adduct over this time scale with ν_{CO} absorptions appearing at 1987 and 1811 cm^{-1}. We have also examined the reaction

12

of 4 equiv. of dry CS_2 with $Na_2[Fe(CO)_5] \cdot 1.5p$-dioxane in THF at 25°C, and although this results in an immediate reaction to give an intense deep red-brown solution, there was no infrared evidence after 21 hr for formation of $[Fe(CO)_5(CS)]$[35] and no tractable organometallic products could be isolated from the reaction mixture.
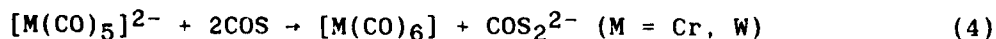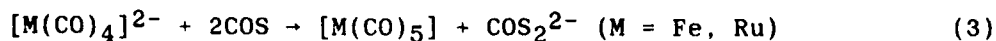
Reduction of Carbonyl Sulfide by Dianionic Carbonyl Metalates. Since S^{2-} is a weaker base than O^{2-}[36] it would also be expected to be a better leaving group,[37] and the failure to observe reduction of CS_2 by representative dianionic carbonyl metalates of the group 6 and 8 metals therefore suggested that formation of the strong CO triple bond provides an important component of the driving force for the observed reductive disproportionation of CO_2 by these dianions. Consistent with this, sodium salts of tetracarbonyl dianions of the group 8 metals ($[Fe(CO)_4]^{2-}$ and $[Ru(CO)_4]^{2-}$) and pentacarbonyl dianions of the group 6 metals ($[Cr(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$) reacted readily with COS to give the corresponding pentacarbonyls and hexacarbonyls as summarized by the data in Table I.

The reactions were initially monitored by solution IR, and spectroscopic yields of $[Fe(CO)_5]$ and $[W(CO)_6]$ were determined by absorbance mode IR. Determination of isolated product yields was, however, difficult in all four cases: $[Fe(CO)_5]$ is a volatile liquid, $[Ru(CO)_5]$ is unstable with respect to $[Ru_3(CO)_{12}]$,[26] and $[Cr(CO)_6]$ and $[W(CO)_6]$ are volatile and difficult to separate from the naphthalene present as a byproduct of the naphthalenide reduction used to prepare the pentacarbonyl dianions. These problems could, however, be circumvented in each case by chemical derivatization – the group 8 pentacarbonyls were oxidized with I_2 to the more stable and less volatile diiodides cis-$[M(CO)_4I_2]$,[25,26] while the hexacarbonyls of the group 6 metals

13

were converted to the corresponding pentacarbonyl bromide anions by oxidative removal of CO with Me_3NO in the presence of $[N(n-Bu)_4]Br$. It did, however, also prove possible to isolate the pure carbonyl in the case of $[W(CO)_6]$, and the 61% yield obtained was comparable to that indicated by the chemical derivatization method.

We have previously established that reduction of carbon dioxide to coordinated carbon monoxide by dianionic carbonyl metalates of the group 6 and group 8 metals is accompanied by the formation of equivalent quantities of carbonate ion.[3] This would suggest that the reactions of these dianions with COS should be accompanied by equimolar formation of $Na_2[COS_2]$ - dithiocarbonate salts are, however, unstable with respect to disproportionation to carbonate and trithiocarbonate,[38] and this complicated analysis of the inorganic products of the reaction, although mull IR spectra of the precipitates from the crude reaction mixtures did contain broad absorptions at 1440 cm^{-1} matching those of $Na_2[CO)_3]$, and a sharper band at 904 cm^{-1} comparable to the principle absorption of an authentic sample of $Na_2[CS_3] \cdot H_2O$. The quantities of these precipitates were consistent with those anticipated, suggesting the stoichiometries in Eq. 3 and 4.

$$[M(CO)_4]^{2-} + 2COS \rightarrow [M(CO)_5] + COS_2^{2-} \quad (M = Fe, Ru) \qquad (3)$$

$$[M(CO)_5]^{2-} + 2COS \rightarrow [M(CO)_6] + COS_2^{2-} \quad (M = Cr, W) \qquad (4)$$

Attempts to spectroscopically observe an intermediate η^1-COS complex in a reduction reaction were only marginally successful. When one equivalent of COS was gradually condensed into a -78°C solution containing $Li_2[W(CO)_5]$ the reaction mixture immediately faded to an orange yellow color. IR spectra indicated the presence of $[W(CO)_6]$, but also had absorptions at 1884 (vs) and 1859 (m) cm^{-1} indicative of a more electron-rich intermediate complex. The

positions and intensities of these absorptions are similar to those which we previously reported for the carbonyl stretching absorptions of $Li_2[W(CO)_5(CO_2)]$,[3] consistent with formulation of this species as $Li_2[W(CO)_5(COS)]$, but the thermally unstable species could not be prepared without considerable contamination by $[W(CO)_6]$, suggesting that it is so reactive that it reacts with incoming COS as fast as it is formed. The observation of an intermediate in reactions using one equiv of COS does, however, support the stoichiometry in Eq. 4, and argue against direct sulfide extrusion from a COS complex.

The reactions of COS with dianionic carbonylmetalates are very sensitive to the presence of water in the COS, and we found it essential to dry commercial COS (see Experimental Section). Undried COS resulted in protonation of the dianions to form hydrido monoanions $[M(CO)_4H]^-$ (M = Fe[39] or Ru[40]) or $[M(CO)_5H]^-$ (M = Cr[41] or W[42]). In the case of the group 8 metals IR indicated that the hydrides were unreactive towards COS, while in the case of the group 6 metals they resulted in competitive formation of the monothioformate complexes $Na[M(CO)_5SC(O)H]$, presumably by insertion into the metal hydride bonds.[27,29]

Reduction of Thioisocyanates with Dianionic Carbonyl Metalates. Results to this point suggested that sulfide could be extracted from dianionic η^1-heteroallene complexes by excess heteroallene as long as the reaction generated a CX triple bond. Since the C≡N bond (ca. 212 kcal mol^{-1}[43]) is intermediate in strength between the C≡O band (256 kcal mol^{-1}[43]) and the C≡S bond (166 kcal mol^{-1}[44]), it seemed possible that reductive disproportionation of thioisocyanates could provide a clean route to mono-isonitrile complexes, and we therefore investigated the reaction of tetracarbonyl dianions of the group 8 metals and pentacarbonyl dianions of the group 6 metals with phenyl thioisocyanate and methyl thioisocyanate.

15

The most promising thioisocyanate reductions were those with Collman's reagent. A suspension of $Na_2[Fe(CO)_4] \cdot 1-5p$-dioxane in THF reacted with 2 equiv of PhNCS over about 1 hr to give a dark precipitate under a deep red solution, from which the known isonitrile complex $[Fe(CO)_4(CNC_6H_5)]$[31] could be isolated in 42% yield. The previous thermal route to this complex gives the product in only moderate yields, and reductive disproportionation of PhNCS provides a competitive route to this material. An analogous reaction of Collman's reagent with CH_3NCS again led to the mono-isonitrile complex $([Fe(CO)_4(CNCH_3)]$[31] but the yield from the alkyl thioisocyanate was not as good as it had been fromthe aryl thioisocyanate, and the product could only be isolated in 24% yield.

In both cases IR spectra indicated quantitative consumption of the 2 equiv of thioisocyanate used in the reaction, consistent with description of the reaction as reductive disproportionations of the heter. ilene by the dianionic carbonylmetalate (Eq. 5). The final fate of the dithiocarbimate which we would expect to be the coproduct was not, however, determined, and the reaction is not general for all R – only traces (IR) of $[Fe(CO)_4(CNtBu)]$[31] were formed when excess tBuNCS was refluxed with $Na_2[Fe(CO)_4] \cdot 1.5$ p-dioxane in THF for 18 h.

$$Na_2[Fe(CO)_4] + 2RNCS \rightarrow [Fe(CO)_4(CNR)] + Na_2[RNCS_2] \qquad (5)$$
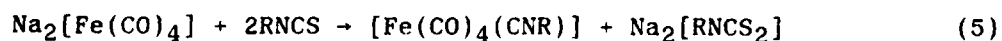
Attempts to extend the Collman's reagent reactions to the reduction of PhNCS with $Na_2[Ru(CO)_4]$ did not lead to a Ru isonitrile complex, and solution IR spectra of the deep red suspension obtained after 11 hr at ambient temperatures indicated the presence of unreacted PhNCS and the formation of an unidentified carbonyl containing compound with absorptions at 2060 (vw), 2005 (s), 1982 (s), and 1933 (s,br) cm^{-1}. No tractable organometallic product could be isolated from the solution.

16

The reactions of thioisocyanates with the pentacarbonylmetalates of the group 6 metals were less experimentally straightforward than the reactions with $[Fe(CO)_4]^{2-}$.
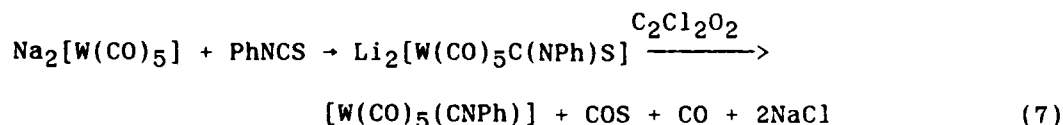
Solutions of $Li_2[Cr(CO)_5]$ did react with 2 equiv of PhNCS over 2 days to give the mono-isonitrile complex $[Cr(CO)_5(CNC_6H_5)]$,[31] but isolated yields were only modest (14%). IR spectra of the crude product suggested that the initial yield was significantly higher, but the fractional sublimination required to separate the complex from naphthalene resulted in significant purification losses.

$$Li_2[Cr(CO)_5] + 2PhNCS \rightarrow [Cr(CO)_5(CNPh)] + Li_2[PhNCS_2] \qquad (6)$$
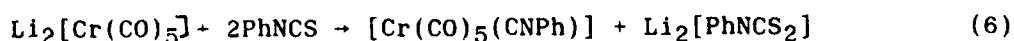
Addition of methyl CH_3NCS (6 equiv) to a solution of $Li_2[W(CO)_5]$ also resulted in consumption of the starting dianion (IR) and ν_{CO} absorptions appeared consistent with the formation of a mono-isonitrile, $[W(CO)_5(CNCH_3)]$,[32] as the major carbonyl containing product, while no absorptions attributable to $[W(CO)_5(CS)]$[33] were observed, but the similar solubilities and volatilities of naphthalene and the mono-isonitrile complex rendered isolation of the latter impractical.

The reaction of $Li_2[W(CO)_5]$ with excess PhNCS was surprisingly complex. Addition of the heteroallene to a solution of the salt at -78°C produced a homogeneous deep red solution whose color intensified as the reaction warmed to 25°C. There was, however, no precipitation of an insoluble inorganic product, and solution IR spectra (although they confirmed consumption of the penta-carbonyl dianion) give no indication that $[W(CO)_5(CNC_6H_5)]$[32] had been formed and no tractable inorganic product could be isolated from this solution. It seemed probable that $[W(CO)_5]^{2-}$ had formed a η^1 complex with the added PhNCS, and we therefore attempted a reaction analogous to that reported by Fehlhammer et al. for the Cr system,[19] and added oxalylchloride to the solution formed by

17

addition of 0.9 equiv of PhNCS to a solution of $Na_2[W(CO)_5]$ in THF at $-78°C$. IR spectra of the initial adduct were strikingly similar to those for the reaction of $Li_2[W(CO)_5]$ with excess PhNCS, and subsequent spectra indicated that this adduct reacted with oxalylchloride to yield a mixture of the anticipated isonitrile complex $[W(CO)_5(CNC_6H_5)]$[32] (Eq. 7) and an unidentified species with ν_{CO} absorptions at 1927 (vs) and 1886 (sh) cm^{-1}. The true yield of the isonitrile complex was probably ca. 20%, but spectroscopically pure product could only be isolated in 6% yield because of losses during sublimation.

$$Na_2[W(CO)_5] + PhNCS \rightarrow Li_2[W(CO)_5C(NPh)S] \xrightarrow{\text{ } C_2Cl_2O_2 \text{ }}$$

$$[W(CO)_5(CNPh)] + COS + CO + 2NaCl \qquad (7)$$

Reactions of Isocyanates with Dianionic Carbonyl Metalates. The observation that isonitriles were the only observable products from the reactions of thioisocyanates with dianionic carbonylmetalates, and that there was no tendency to form thiocarbonyl complexes, is consistent with the expectation that the direction of reduction of asymmetric heteroallenes is predominantly controlled by the strength of the triple bond in the C≡X ligand being formed. As pointed out above, however, the C≡N bond, although weaker than a C≡C bond, is much stronger than a C≡S bond, and this raised the possibility that there might not be a strong preference in the direction of reduction of asymmetric heteroallenes in which there were oxo and imido groups at the ends of the heteroallenes. We therefore examined the reactions of aryl and alkyl isocyanates with representative dianionic carbonylmetalates of the group 6 and 8 metals.

As expected, $[W(CO)_6]$ was the principal product of the reaction of phenyl isocyanate (4 equiv) with $Na_2[W(CO)_5]$ in THF with $-78°C$. This gave a pale yellow suspension, followed by a homogeneous yellow solution after the mixture had

18

warmed to ambient temperatures. IR spectroscopy established that $[W(CO)_6]$ was the dominant tungsten complex in this solution, together with smaller quantities of $[W(CO)_5(CNC_6H_5)]$,[32] and after the addition of a second portion of PhNCO (2 equiv) to ensure complete reaction absorbance mode IR indicated solution yields of 84% $[W(CO)_6]$ and 5% $[W(CO)_5(CNPh)]$.

The most reasonable stoichiometry for the reaction by which the $[W(CO)_6]$ had been formed is that in Eq. 8, but direct evidence for the consumption of 2 equiv. of the isocyanate is lacking. PhNCO tends to trimerize to N,N',N"-triphenylisocyanurate,[45] and IR spectra of the crude reaction mixture, which indicated complete consumption of the initial 4 equiv of PhNCO, also exhibited a moderately strong absorption at 1712 cm^{-1} which suggested formation of significant quantities of the cyclic trimer.

$$Na_2[W(CO)_5] + 2PhNCO \rightarrow [W(CO)_6] + Na_2[(PhN)_2CO] \qquad (8)$$
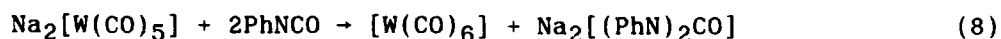
Competitive cyclotrimerization was an even more significant problem with the group 8 metals, and three was no observable reduction of CH_3NO or PhNCO by Collman's reagent. Addition of either heteroallene (6 equiv) to a THF suspension of Collman's reagent at 25°C led exclusively to cyclotrimerization,[45,46] suggesting that cyclotrimerization is faster than addition to $[Fe(CO)_4]^{2-}$.

Reactions of Carbodiimides with Collman's Reagent. The reduction of carbodiimides potentially provides an alternative approach to mono-isonitrile complexes, but experiments with Collman's reagent suggested that this was not, in practice, a useful reaction. Although the reaction of $Na_2[Fe(CO)_4]\cdot1.5$ p-dioxane with PhNCNPh did lead to the formation of $[Fe(CO)_4(CNPh)]$, the isolated yield was small (10 %), and, since similar experiments with the cyclohexyl analog $C_6H_{11}NCNC_6H_{11}$ did not lead to detectable levels of $[Fe(CO)_4(CNC_6H_{11})]$ after 6.5 h at 25°C, no further experiments were conducted with carbodiimides.

19

Conclusion

The results above establish that dianionic carbonylmetalates of the group 6 and group 8 metals can reduce a number of heteroallenes $X=C=Y$ other than CO_2 to coordinated $C\equiv X$ ligands, provided X is a first row element (N or O) which can form a strong triple bond with C. We have, for example, seen no cases of formation of a coordinated thiocarbonyl, and the marked preference for the formation of carbonyl ligands rather than isonitriles (as shown by the reaction of $Na_2[W(CO)_5]$ with PhNCO and by the higher yields of carbonyl complexes from reactions with COS than of isonitriles from reduction of thioisocyanates) is consistent with control of the direction of reduction of asymmetric heteroallenes by the relative strengths of the $C\equiv X$ bands formed. The failure to observe reductive disproportionation of CS_2 would suggest that the strength of the $C=X$ bond being cleaved is not an important factor, since the $C=S$ bond is weaker than the $C=N$ and $C=O$ bonds, but we cannot rule out the possibility that the strength of the M–C bonds being formed is important, since these are likely to increase in a sequence (M–CO > M–CNR > M–CS) which parallels the strength of the $C\equiv X$ triple bonds.

Footnotes

(1) Taken in part from the Ph.D. Thesis of Dr. Gary R. Lee, Harvard University, 1985

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23

TABLE I. Characterized Organometallic Products from the Reductions of Carbonyl
Sulfide, Thioisocyanates, Isocyanates and Carbodiimides with
Dianionic Carbonylmetalates

Heteroallene	Dianionic Carbonylmetalate	Initial Product (Solution Yield)	Isolated Product (Yield)
COS	$Na_2[Fe(CO)_4]$	$[Fe(CO)_5]$ (73%)	$[Fe(CO)_4I_2]$ (72%)
COS	$Na_2[Ru(CO)_4]$	$[Ru(CO)_5]$	$[Ru(CO)_4I_2]$ (72%)
COS	$Na_2[Cr(CO)_5]$	$[Cr(CO)_6]$	$[N(n\text{-}Bu)_4][Cr(CO)_5Br]$ (82%)
COS	$Na_2[W(CO)_5]$	$[W(CO)_6]$ (74%)	$[N(n\text{-}Bu)_4][W(CO)_5Br]$ (57%)
COS	$Na_2[W(CO)_5]$	$[W(CO)_6]$	$[W(CO)_6]$ (61%)
PhNCS	$Na_2[Fe(CO)_4]$	----	$[Fe(CO)_4(CNPh)]$ (42%)
MeNCS	$Na_2[Fe(CO)_4]$	$[Fe(CO)_4(CNCH_3)]$	$[Fe(CO)_4(CNCH_3)]$ (24%)
PhNCS	$Li_2[Cr(CO)_5]$	----	$[Cr(CO)_5(CNPh)]$ (14%)
PhNCO	$Na_2[W(CO)_5]$	$[W(CO)_6]$ (84%) $+ [W(CO)_5(CNPh)]$ (7%)	----
PhNCHPh	$Na_2[Fe(CO)_4]$	-----	$[Fe(CO)_4(CNPh)]$ (10%)

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