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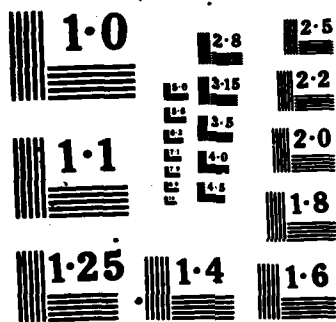
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The Formation of Metalloicycloimides from the  
Reaction of Isocyanates with a Neutral  
Transition Metal Carbonyl

by

Peter Jernakoff and N. John Cooper

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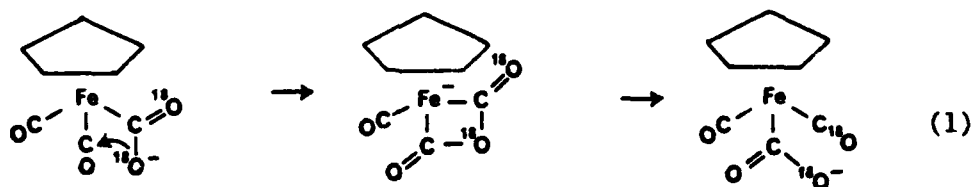
Abstract (for Chemical Abstracts).

The nucleophilic carbonyl complex  $[W(\eta^5-C_5H_5)_2(CO)]$  (1) reacts readily with the isocyanates  $OCNR$  ( $R = CH_3, Ph$ ) in pentane to give the first reported metallocycloimides  $[W(\eta^5-C_5H_5)_2\{C(O)N(CH_3)C(O)\}]$  (2) and  $[W(\eta^5-C_5H_5)_2\{C(O)N(Ph)C(O)\}]$  (3). It is suggested that the reaction involves initial  $\eta^5-C$  coordination of an isocyanate to give a zwitterionic intermediate in which the ligands are simultaneously activated in opposite senses, and that nucleophilic attack by the heteroallene on the electrophilic carbonyl then gives a metallocycloimide. Complex 2 has been structurally characterized by a single crystal X-ray diffraction study (monoclinic space group  $P2_1/m$ , with  $Z = 2$ ;  $a = 7.6586 \text{ \AA}$ ,  $b = 8.6718 \text{ \AA}$ ,  $c = 9.6557 \text{ \AA}$ ;  $\beta = 101.45^\circ$ ;  $d_{calc} = 2.20 \text{ g/cc}$ ;  $R = 2.20 \%$  and  $R_w = 2.19 \%$ ) which establishes that the metallocycloimide group is essentially planar. Both 2 and 3 are moderately water sensitive, regenerating 1 at  $55^\circ C$  and ambient temperatures respectively. Complex 1 in toluene does not react with 1.7 atmospheres of  $CO_2$  at temperatures up to  $85^\circ C$ .

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We have recently reported that the activation of CO<sub>2</sub> by η<sup>1</sup>-C complexation to [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>-</sup> results in facile oxygen exchange between coordinated CO<sub>2</sub> and coordinated CO,<sup>1</sup> and we have suggested that these exchanges follow attack by a nucleophilic oxygen of the CO<sub>2</sub> ligand on a neighboring carbonyl ligand (Eq. 1). This would give a transient metalloanhydride analogous to the metalloheterocycles which Fehlhammer has previously reported to be major or minor products of the reactions of [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>-</sup> with carbodiimides,<sup>2</sup> isothiocyanates,<sup>3</sup> and ketenimines.<sup>4</sup> The lability of the metalloanhydrides in this anionic system may reflect the replacement of two good π-acceptor ligands (CO and the η<sup>1</sup>-CO<sub>2</sub>) with a poor π-acceptor ligand, and more stable metalloheterocycles might be anticipated from the addition of heteroallenes to carbonyl complexes which are sufficiently electron rich to activate the heteroallenes but which do not carry a negative charge.<sup>5</sup> We now wish to report the successful application of this approach to the synthesis of the first metallocycloimide complexes by reaction of isocyanates with a neutral carbonyl complex.

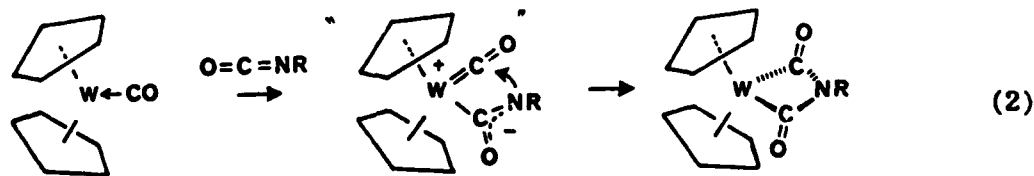


The facile oxidative addition of alkyl, allyl and acyl halides<sup>6</sup> to [W(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)]<sup>7</sup> (1) indicates that 1 is an exceptionally nucleophilic neutral carbonyl complex and a promising substrate for the addition of heteroallenes. We began by examining the reaction of 1 with isocyanates. Addition of methylisocyanate (13.0 mL, 220 mmol) to an intensely green slurry of [W(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)] (0.648 g, 1.90 mmol) in pentane (60 mL) led over 1 h to the formation of an orange solution and the precipitation of a bright orange powder. The supernatant was decanted off and the powder washed with pentane and vacuum dried to give 0.667 g (1.67 mmol = 87 %) of spectroscopically pure [W(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>{C(O)N(CH<sub>3</sub>)C(O)}] (2). Analytically pure material could be obtained as irregular needles (ca. 90 % recovery) by slow cooling of a saturated acetone solution of the complex to -78°C.<sup>8</sup>

The metallocycloimide structure of 2 was established by a single crystal X-ray diffraction study of the bright orange cubes obtained by cooling a saturated acetone (reagent grade) solution of the material to 0°C over a 4 h period.<sup>9,10</sup> The molecular structure of 2 is shown in Figure 1. The metallocycle core of the molecule is close to what would be expected by comparison with the structures of typical cyclic imides,<sup>11</sup> and the metal atom, the ring carbon atoms, and the nitrogen atom are essentially coplanar. The trigonal geometry of the nitrogen atom,<sup>12</sup> together with the short nitrogen-ring carbon bond lengths of 1.393 (4) Å, indicates that the nitrogen lone pair is delocalized over the two carbonyl carbons.

Formation of metallocycloimides from 1 is not restricted to the reaction with methylisocyanate, and a slurry of 1 (0.284 g, 0.83 mmol) in pentane (30 mL) reacted immediately with excess PhNCO (2.0 mL, 18.3 mmol) to give an orange solution and a pale orange powder. After 1 h the supernatant was decanted off and the precipitate washed with pentane and vacuum dried to give 0.331 g (0.72 mmol  $\equiv$  87 %) of analytically pure  $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{O})\}]$  (3)<sup>13</sup>.

The most reasonable mechanism for the formation of 2 and 3 involves initial  $\eta^1\text{-C}$  coordination of a Lewis acidic isocyanate to the basic metal center (Eq. 2). In such a zwitterionic intermediate the heteroallene and the carbonyl ligand are simultaneously activated in opposite senses: the heteroatoms are rendered nucleophilic and the unsaturated carbonyl carbon electrophilic, leading to ring closure to give a metalloheterocycle. The dominant factor dictating ring closure through nitrogen rather than through oxygen is probably the thermodynamic preference for forming C=O bonds rather than C=N bonds: the isomeric metalloisoimide contains one C=O and one C=N bond in place of the two C=O bonds in 2 and 3.<sup>14</sup>



R = Me, Ph

Although the mechanism in Eq. 2 would suggest that metallocycloimides might

be formed from many carbonyl substrates, we have discovered no other reports of metalloheterocycle formation from the reaction of isocyanates, nor indeed of any other heteroallene, with neutral carbonyl complexes. There is, however, an early report of the formation of isocyanide complexes from the reaction of isocyanates with carbonyls of the Group 6 and 8 metals,<sup>15</sup> and a subsequent report of the use of this reaction as the first step in the catalytic conversion of isocyanates to carbodiimides and CO<sub>2</sub>.<sup>16</sup> It seems reasonable to assume that these reactions proceed through metallocycloisoimides related to 2 and 3, and both these and metallocycloimides may be more generally accessible than the existing literature would suggest.

Hydrolysis of the metallocycloimides provides an interesting contrast with the hydrolysis of cyclic organic imides,<sup>17</sup> and does not require basic or acidic catalysis. Treatment of a THF solution of 3 with a large excess of water results in essentially complete regeneration of  $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  in one day. The N-phenyl complex 3 is more water sensitive than the N-methyl complex 2 (presumably, as in the case of organic analogues, as a result of conjugation of the N lone pair with the phenyl ring<sup>17</sup>), and no 1 was formed when the methyl complex 2 was treated for 1 day with excess water in acetone at ambient temperatures. Complex 2 was, however, essentially quantitatively converted to 1 when the mixture was heated to 55°C for 20 h.

Hydrolysis of cyclic organic imides typically gives amidic acids,<sup>17</sup> and tungstena analogues of such species (A) are reasonable intermediates in the hydrolysis of 2 and 3 (Scheme I). The details of the conversion of A to 1 are, however, unclear at this point. Argument by analogy with detailed studies of the hydrolysis of phthalmic acid<sup>18</sup> suggests the intermediacy of the metalloanhydride B and argues against direct hydrolysis of A to the metallocarboxylic acid C, but B may still be converted to 1 through C rather than by direct loss of CO<sub>2</sub>.<sup>19</sup>

The metallocycloimides 2 and 3 are the closest analogues of a metalloanhydride isolated to date, but attempts to extend the reaction of 1 with heteroallenes to the preparation of B itself have so far been unsuccessful. Complex 1 in toluene solution

was inert to 1.7 atmospheres of CO<sub>2</sub> (65 equiv) at temperatures up to 85°C, and evidence against the possibility that B is a kinetically accessible but unstable intermediate came from an experiment in which a toluene solution of 1 was heated at 65°C for 3 h under 6.5 equivalents of <sup>13</sup>CO<sub>2</sub> at a pressure of ca. 0.14 atmospheres. The recovered 1 contained none of the <sup>13</sup>CO (mass and IR spectroscopy) which would be anticipated if B formed transiently and then collapsed back to 1 and free CO<sub>2</sub>, and we conclude that the exceptional stability of CO<sub>2</sub> precludes in this system a sequence involving CO<sub>2</sub> analogous to that in Eq. 2.

**Acknowledgments** We thank the Office of Naval Research for financial support. We thank Dr. Donald Wink and Dr. Jim Fox for assistance with the X-ray diffraction study. The Nicolet R3 diffractometer and Bruker spectrometers used were purchased with the aid of grants to Harvard University from the NSF.

**Supplementary Material Available:** Figures showing full atomic numbering scheme and packing within the unit cell together with tables of atomic positional and thermal parameters, intramolecular bond lengths and angles, least squares planes, interplanar angles, angles about tungsten, and structure factors (18 pages). Ordering information is given on any masthead page.

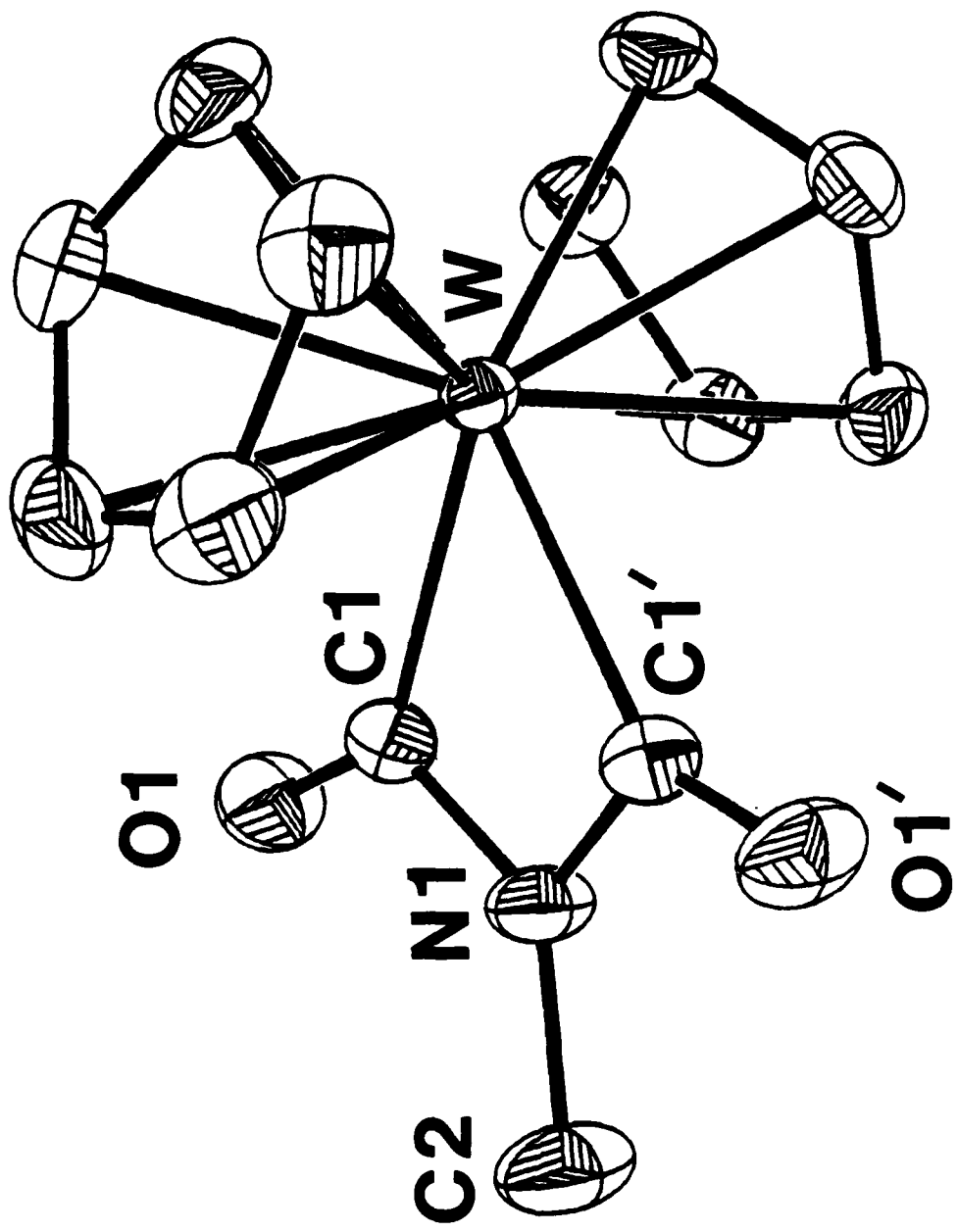
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- (8)  $^1\text{H}$  NMR (acetone- $d_6$ , 300.13 Mhz)  $\delta$  4.95 (s, 10,  $2\text{C}_5\text{H}_5$ ), 2.31 (s, 3,  $\text{NCH}_3$ );  $^{13}\text{C}$  NMR (DMSO- $d_6$ , gated decoupled, 75.47 Mhz)  $\delta$  176.2 (s, satellites  $J_{\text{W-C}} = 93.4$  Hz,  $\text{C=O}$ ), 86.3 (d,  $J = 183$  Hz,  $\text{C}_5\text{H}_5$ ), 22.8 (q,  $J = 138$  Hz,  $\text{CH}_3$ ); mass spectrum (parent ion,  $^{184}\text{W}$ ),  $m/e$  399. Anal. Calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{W}$ : C, 39.12; H, 3.29; N, 3.51. Found (Schwarzkopf Laboratories, NY; sample dried at  $10^{-4}$  mm Hg for 24 h to remove occluded  $\text{H}_2\text{O}$ ): C, 39.06; H, 3.37; N, 3.58.
- (9) The diffraction study revealed the presence of one molecule of water of crystallization per molecule of 2 (IR confirmed the presence of  $\text{H}_2\text{O}$  in a bulk sample of the orange cubes and its absence from analytical samples). Crystal data: monoclinic space group  $\text{P}2_1/\text{m}$ ,  $Z = 2$ ,  $a = 7.659$  (2) Å,  $b = 8.672$  (2) Å,  $c = 9.656$  (2) Å,  $\beta = 101.45$  (2) $^\circ$ ,  $d_{\text{calc}} = 2.20$  g/cc,  $\mu = 97.1$   $\text{cm}^{-1}$ ,  $\lambda(\text{MoK}\alpha) = 0.71069$  Å. Of the 3158 reflections measured in the range

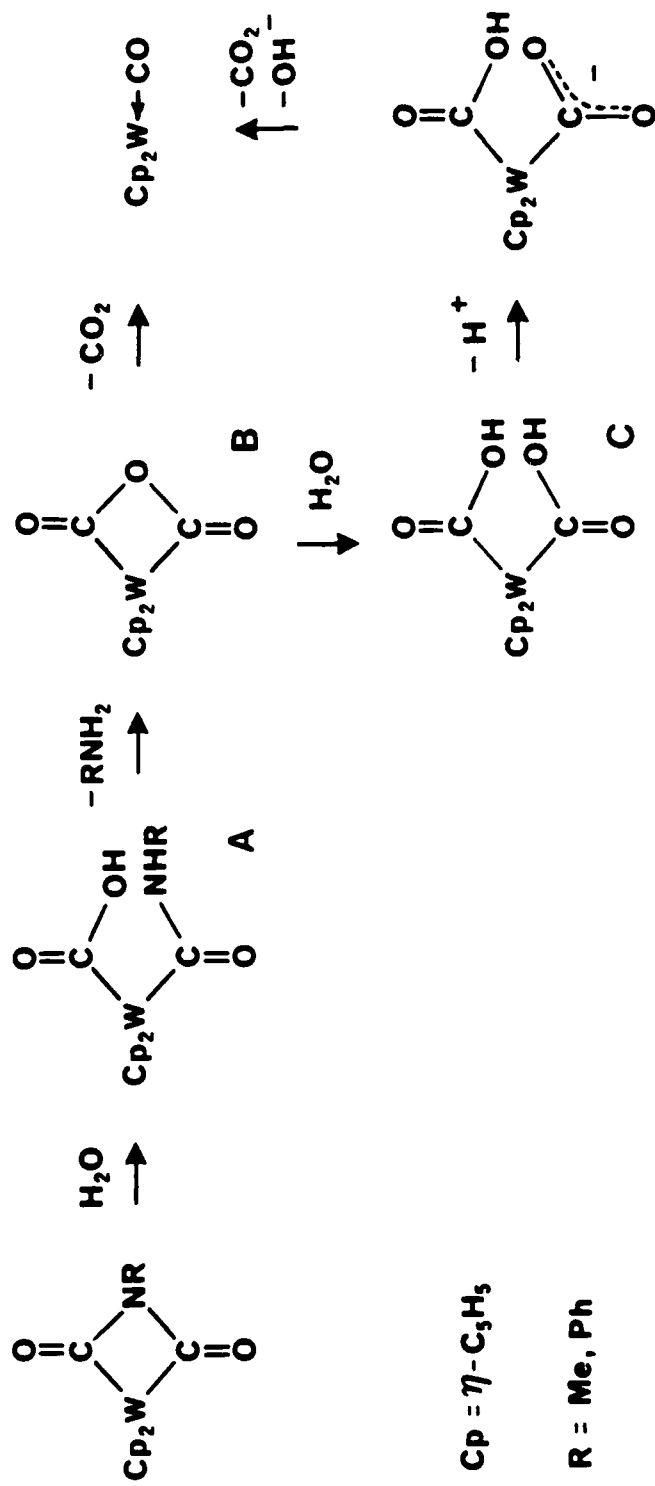
$3^\circ \leq 2\theta \leq 60^\circ$  on a Nicolet R3 four circle diffractometer, 1881 unique reflections with  $I > 3\sigma$  were used in the structure solution (Patterson) and refinement (SHELXTL).<sup>10</sup> Least squares refinement with a block diagonalized matrix converged at  $R = 2.20\%$  and  $R_w = 2.19\%$ . The hydrogens of the water molecule were not located, and all other hydrogen atoms were placed in calculated positions. The largest unassigned peak in the final difference map ( $0.88 \text{ e}^-/\text{A}^3$ ) was located 0.91 Å from the oxygen atom of the water.

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- (12) The nitrogen atom is only 0.041 Å above the plane defined by C(1), C(2), and C(1')
- (13)  $^1\text{H}$  NMR (acetone- $d_6$ , 300.13 Mhz)  $\delta$  7.42-7.36, 7.26-7.18, 7.10-7.03 (m, 5,  $\text{C}_6\text{H}_5$ ), 5.10 (s, 10,  $2\text{C}_5\text{H}_5$ );  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 75.47 Mhz)  $\delta$  176.6 (s, satellites  $J_{\text{w-c}} = 91.6 \text{ Hz}$ , C=O), 134.5 (s,  $\text{C}_6\text{H}_5$ ), 128.6 (s,  $\text{C}_6\text{H}_5$ ), 126.0 (s,  $\text{C}_6\text{H}_5$ ), 123.7 (s,  $\text{C}_6\text{H}_5$ ), 84.4 (s,  $\text{C}_5\text{H}_5$ ). Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{W}$ : C, 46.87; H, 3.28; N, 3.04. Found (Galbraith Laboratories, TN): C, 47.10; H, 3.30; N, 3.15.
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- (19) The formation of aniline and  $\text{CO}_2$  after partial hydrolysis of 3 was confirmed by  $^1\text{H}$  NMR (aniline) and GC ( $\text{CO}_2$ ) analysis of a sample in  $d_6$  acetone.

**Figure 1.** Molecular structure of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]$  (50% probability ellipsoids). Primed atoms are symmetry generated by the plane through the W and N atoms perpendicular to the metallocycloimide plane. Selected bond lengths (Å) and angles (deg): W-C(1) = 2.195 (3), C(1)-O(1) = 1.213 (5), C(1)-N(1) = 1.393 (4), N(1)-C(2) = 1.451 (7); C(1)-W-C(1') = 60.3 (2), W-C(1)-N(1) = 97.4 (2), C(1)-N(1)-C(1') = 104.7 (4), C(1)-N(1)-C(2) = 127.5 (2), W-C(1)-O(1) = 139.4 (3).

**Scheme I.** Possible mechanisms for the solvolysis of the metallocycloimides 2 and 3 to the carbonyl complex 1.





Scheme I. Possible mechanisms for the solvolysis of the metallocycloimides 2 and 3 to the carbonyl complex 1.

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