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Catalytic Oxidation of Phosphines by
Transition Metal-Activated Carbon Dioxide

by

Kenneth M. Nicholas

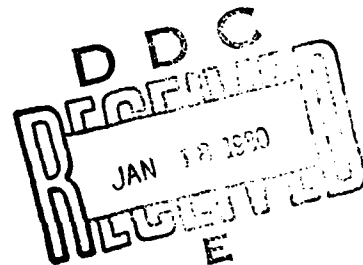
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CATALYTIC OXIDATION OF PHOSPHINES BY TRANSITION
METAL-ACTIVATED CARBON DIOXIDE

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Summary

The complexes $(\text{Ph}_3\text{P})_3\text{RhCl}$ and $[(\text{cyclooctene})_2\text{RhCl}]_2$ have been found to catalyze the oxidation of phosphines by carbon dioxide in refluxing decalin. The rate of oxidation increases in the order $\text{PPh}_3 < \text{PBuPh}_2 < \text{PEt}_3$.

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As the world's petroleum reserves dwindle, there is an intensive search underway for alternative fuels and organic feedstocks. This has stimulated considerable interest in the potential activation of carbon dioxide by means of transition metal complexes¹. Although a few discreet CO₂ complexes have been reported²⁻⁷, in several cases, reactions of carbon dioxide with metal complexes have yielded carbonyl and carbonate or oxide species - products of CO₂ disproportionation⁷⁻¹¹. In a few instances, e.g. in reactions of CO₂ with (C₂H₄)Mo(diphos)₂¹² and (R₃P)₃RhCl¹³, stoichiometric O-atom transfer to phosphine apparently occurs, producing phosphine oxide, either free or coordinated. We now report that under appropriate conditions, phosphines can be oxidized by carbon dioxide catalytically in the presence of [(cyclooctene)₂RhCl]₂ or (Ph₃P)₃RhCl (eq. 1).



When a decalin solution of triphenylphosphine containing one mole % of (Ph₃P)RhCl or [(C₈H₁₄)₂RhCl]₂ is refluxed (ca. 185°C) under an atmosphere of purified CO₂^{*}, triphenylphosphine oxide is slowly produced (turnover number ca. 20/day) as indicated by the growth of IR bands at 1210, 1115, and 720cm⁻¹^{**}. After several days, high yields of Ph₃PO (m.p. 148-151°C, lit¹⁶ 150-152) could be obtained upon cooling the mixture. The co-production of CO was confirmed by the gradual formation of a MnO₂/Ag precipitate when

*"Bone dry" grade CO₂ was passed first through a Cr(II)/HClO₄ solution, then through a dry ice trap, and finally over 3A molecular sieves.

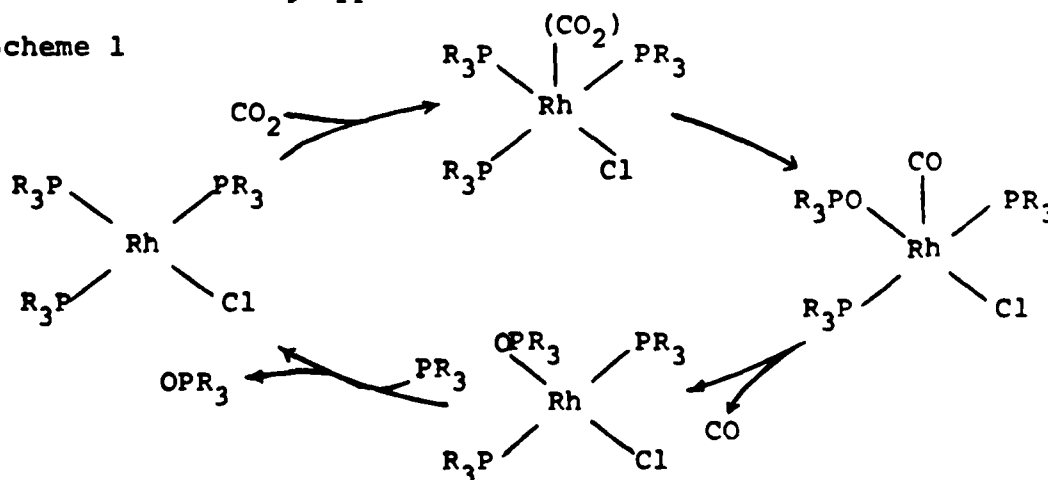
**No reaction was observed in the absence of (PPh₃)₃RhCl or under a nitrogen atmosphere.

the exit gases were passed through an aqueous $\text{KMnO}_4/\text{AgNO}_3$ solution¹⁷.

Other phosphines are also oxidized under these conditions and qualitatively, the rate of reaction parallels the phosphine basicity. Thus, while the oxidation of PPh_3 was complete only after 7-8 days, PBuPh_2 was totally converted to OPBuPh_2 after 3 days, and PEt_3 to OPEt_3 in less than 44 hrs.

We do not as yet have any direct mechanistic information on these reactions and so any proposed mechanisms at present are best considered somewhat speculative. However, in view of the reported conversion of $(\text{R}_3\text{P})_2\text{Rh}(\text{CO}_2)\text{Cl}$ to $(\text{R}_3\text{P})(\text{R}_3\text{PO})\text{Rh}(\text{CO})\text{Cl}$ ¹³ and our observation of the lesser catalytic activity of $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$ compared to $(\text{PPh}_3)_3\text{RhCl}$ (precluding the intermediacy of the former), we suggest the following scheme as a reasonable working hypothesis.

Scheme 1



Kinetic studies are in progress as are efforts to establish the scope of transition metal-mediated CO_2 oxidations with other catalysts and substrates.

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References

1. For a recent review see: M.E. Volpin and L.S. Kolominikov, Organometallic Reactions, vol. 5, 313 (1975);
2. M. Aresta, C.F. Nobile, V.G. Albano, E. Forni, M. Manassero, Chem. Comm., 636 (1975).
3. M. Aresta and C.F. Nobile, J. Chem. Soc. Dalton, 708 (1977).
4. I.S. Kolminikov, A.I. Gusev, G.G. Alexandrov, T.S. Lobeeva, Y.T. Struckov, and M.E. Volpin, J. Organometal. Chem., 59, 349 (1973).
5. B.R. Flynn and L. Vaska, J. Am. Chem. Soc., 95, 508 (1973).
6. G. Fachinetti, C. Floriani, and P. Zanazzi, ibid, 100, 7403 (1978).
7. T. Herskovitz, J. Am. Chem. Soc., 99, 2391 (1977).
8. J. Chatt, M. Kubota, G. Leigh, F.C. March, R. Mason, and D.J. Yarrow, Chem. Comm., 1033 (1974).
9. S. Krogsrud, S. Komiya, T. Ito, J.A. Ibers, and A. Yamamoto, Inorg. Chem., 15, 2798 (1976).
10. G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, J. Am. Chem. Soc., 101, 1767 (1979).
11. G.O. Evans, W.F. Walter, D.R. Mills, and C.A. Streit, J. Organometal. Chem., 144, C34 (1978).
12. T. Ito and A. Yamamoto, J. Chem. Soc. Dalton, 1398 (1975).
13. M. Aresta and L.F. Nobile, Inorg. Chim. Acta., 24, L 49 (1977).
14. G.M. Kosolapoff, J. Am. Chem. Soc., 64, 2982 (1942).
15. "The Chemists' Companion," A.J. Gordon and R.A. Ford, Wiley and Sons, N.Y., p. 440 (1972).