

Octahedral Metal Carbonyls: Reactions and Bonding. VI^{1a} Derivatives of Some Octahedral Metal Carbonyl Complexes Containing Bidentate Ligands

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The reactions with a variety of monodentate Lewis bases (*L*) of (bidentate) $M(CO)_4$ ($M = Cr, Mo$) complexes in which the bidentate ligand contains amine, phosphine or sulfide functional groups have been investigated. For $(DTH)Cr(CO)_4$ ($DTH = 2,5$ -dithiahexane), $(DTH)Mo(CO)_4$, $(tmen)Cr(CO)_4$ ($tmen = N,N,N',N'$ -tetramethylethylenediamine), $(NP)Cr(CO)_4$ ($NP = 1$ -(diethylamino)-2-(diphenylphosphino)-ethane) and $(NP)Mo(CO)_4$, replacement of the bidentate ligand was observed, with the formation of *cis* or *trans*- $(L)_2M(CO)_4$ or *cis*- $(L)_3M(CO)_3$ products, depending upon the *L* ligand employed. Several new complexes have been prepared through use of this route. The reaction of $(tmen)Mo(CO)_4$ with *L* involves two competitive processes, either replacement of *tmen*, or the replacement of CO to form a «mixed» derivative, *cis*- $(L)(tmen)Mo(CO)_3$, followed by replacement of *tmen*. The partition of the reaction between the two paths is dependent upon the steric nature of *L*. Reactions of $(diphos)Mo(CO)_4$ ($diphos = 1,2$ -bis(diphenylphosphino)ethane) with *L* give «mixed» derivatives of the types *cis* and *trans*- $(L)(diphos)Mo(CO)_3$ and *cis*- $(L)_2(diphos)Mo(CO)_2$, the extent of carbonyl replacement and product stereochemistry again being a function of the ligand employed. The results, together with other data cited from the literature may best be explained in terms of σ as well as π -bonding effects in octahedral metal carbonyl systems.

Introduction

«Mixed» octahedral derivatives – which contain two different non-carbonyl Lewis base substituents – of the Group VIB metal carbonyls, $M(CO)_6$ ($M = Cr, Mo, W$) have been known since 1935,² but recently have been the subject of renewed interest.³ Those thus far

investigated are of the types *cis*- $(L)(bidentate)M(CO)_3$ and $(L)_2(bidentate)M(CO)_2$ ($L =$ various monodentate Lewis bases; bidentate = 2,2'-dipyridyl (dipy) or *o*-phenanthroline (phen) and have been prepared through reaction of $(dipy)M(CO)_4$ or $(phen)M(CO)_4$ with the appropriate monodentate ligand. In the more highly substituted type, *L* ligands evidently occupy *trans* sites. Since all the «mixed» complexes thus far reported contain the very similar bidentate ligands dipy and phen, and since kinetic studies of the reactions of $(dipy)M(CO)_4$ show dipy to exert an unexpected labilizing effect on the unreplaced carbonyl groups,⁴ studies of other «mixed» derivatives – containing bidentate ligands differing in bonding properties from dipy and phen are of interest. The reactions with monodentate ligands of some $(bidentate)Cr(CO)_4$ and $(bidentate)Mo(CO)_4$ complexes in which the bidentate ligands contain amine, phosphine or sulfide functional groups are reported and discussed here.

Experimental Section

A. General. Infrared spectra of the complexes (carbonyl stretching region) were taken using a Perkin Elmer Model 421 grating spectrophotometer and were calibrated against the known bands of polystyrene. Spectra in the metal-carbon stretching region were obtained using a Perkin Elmer 521 instrument. Chemical analyses were performed by Midwest Microanalytical Laboratory, Inc., Indianapolis, Indiana, or by Weiler and Strauss Microanalytical Laboratory, Cambridge, United Kingdom. The Cr analysis for the pyrophoric *cis*- $(C_6H_{11}NH_2)_2Cr(CO)_3$ was performed in this laboratory. Unless otherwise noted, chemicals employed were obtained from commercial sources and were used without further purification. Standard literature procedures were used to obtain the complexes $(DTH)Cr(CO)_4$ and $(DTH)Mo(CO)_4$,⁵ $(tmen)Cr(CO)_4$ and $(tmen)Mo(CO)_4$,⁶ and $(NP)Cr(CO)_4$ and $(NP)Mo$ -

(1) (a) The first five papers in this series: G. R. Dobson, *Inorg. Chem.*, **4**, 1673 (1965); II. L. W. Houk and G. R. Dobson, *J. Chem. Soc., A*, 317 (1966); III. G. R. Dobson, R. C. Taylor and T. D. Walsh, *Chem. Comm.*, 281 (1966); IV. L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966); V. G. R. Dobson, R. C. Taylor and T. D. Walsh, *Inorg. Chem.*, in press. (b) Present address, Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069; to whom all correspondence concerning this paper should be addressed. (c) American Chemical Society - Petroleum Research Fund Fellow (1966-7).
(2) (a) W. Hieber and F. Mühlbauer, *Z. Anorg. Allgem. Chem.*, **221**, 337 (1935). (b) W. Hieber and E. Romberg, *ibid.*, **221**, 349 (1935).
(3) (a) L. W. Houk and G. R. Dobson, *J. Chem. Soc., A*, 317 (1966). (b) L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966), and references cited therein.

(4) (a) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965). (b) J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).
(5) H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962); DTH = 2,5-dithiahexane.
(6) R. Poilblanc, *Compt. Rend.*, **256**, 4910 (1963); *tmen* = N,N,N',N' -tetramethylethylenediamine.

(CO)₄.⁷ Pure (diphos)Mo(CO)₄ was prepared through use of a standard procedure,⁸ followed by recrystallization from hot *n*-heptane until a white product was obtained.

B. Preparation of *cis*-[(C₆H₅)₃Sb]₂Cr(CO)₄, *trans*-[(C₂H₅O)₃P]₂Cr(CO)₄, and related reactions. (DTH)Cr(CO)₄ and a four-fold excess of (C₆H₅)₃Sb were refluxed under nitrogen in dichloroethane for three hours. The solution was then filtered, the solvent removed *in vacuo*, and the yellow crystalline *cis*-[(C₆H₅)₃Sb]₂Cr(CO)₄ was obtained by twice recrystallizing from ice cold dichloroethane-hexane. There was no evidence for the formation of the *trans* isomer. *Anal.* Calc'd for C₄₀H₃₀O₄Sb₂Cr: C, 55.21; H, 3.48. Found: C, 55.46; H, 3.58. Carbonyl stretching frequencies (dichloroethane solution): 2013 (m); 1927 (s); 1906 (s); 1902 (sh) cm⁻¹.

The DTH ligand can be displaced under very mild conditions, and thus it was possible to obtain spectral evidence for *cis*-disubstituted complexes of ligands whose *trans* isomers are formed exclusively under more vigorous reaction conditions. Thus, evidence for the new complex *cis*-[(CH₃)₂N]₂P₂Mo(CO)₄ (ν_{CO} (dichloroethane solution) (2016 (m), 1905 (sh), 1890 (s) cm⁻¹) was obtained; there was no evidence for the formation of the analogous Cr complex. At 42°C a small amount of the previously unreported *cis*-[(C₂H₅O)₃P]₂Cr(CO)₄ is formed, together with the *trans* isomer, as is shown by a high energy band at 2024 cm⁻¹ (dichloroethane). The lower bands are masked by that of the *trans* isomer. (NP)Cr(CO)₄, (NP)Mo(CO)₄ and (tmen)Cr(CO)₄ react in an analogous manner with phosphines and phosphites, with replacement of the bidentate ligand. *Trans*-[(C₂H₅O)₃P]₂Cr(CO)₄ was thus obtained by slowly adding triethyl phosphite to a refluxing mixture of (tmen)Cr(CO)₄ in *n*-heptane. When the reaction mixture became colorless, it was suction filtered, and the filtrate was cooled overnight with dry ice. The colorless crystalline product was collected by suction filtration, washed with small amounts of cold petroleum ether, and dried *in vacuo*. *Anal.* Calc'd for C₁₆H₃₀O₁₀P₂Cr: C, 38.73; H, 6.05; P, 12.49. Found: C, 38.50; H, 5.51; P, 12.66. Carbonyl stretching frequencies (cyclohexane solution): 1965 (w), 1912 (s) cm⁻¹.

C. Preparation of *cis*-(C₆H₁₁NH₂)₃M(CO)₃ (M = Cr, Mo) and related reactions. (Tmen)Mo(CO)₄ was refluxed under nitrogen in cyclohexylamine for fifteen minutes. The cream colored *cis*-(C₆H₁₁NH₂)₃Mo(CO)₃ was obtained by suction filtration, washed with petroleum ether, and dried *in vacuo*. *Anal.* Calc'd for C₂₁H₃₉N₃O₃Mo: C, 52.70; H, 8.23. Found: C, 52.46; H, 8.44. Carbonyl stretching frequencies (nujol mull): 1879 (s), 1730 (vs, br) cm⁻¹. The analogous Cr derivative was obtained similarly as an air-sensitive, pyrophoric, bright yellow powder. *Anal.* Calc'd for C₂₁H₃₉N₃O₃Cr: Cr, 11.99. Found: Cr, 13.29. Carbonyl stretching frequencies (nujol mull): 1872 (s), 1729 (vs, br) cm⁻¹. The high value for the Cr analysis may be attributed to the partial decomposition of the complex

before it could be performed. (Tmen)Mo(CO)₄, (DTH)Cr(CO)₄, (DTH)Mo(CO)₄, (NP)Cr(CO)₄ and (NP)Mo(CO)₄ gave the same two products with cyclohexylamine, and also yield *cis*-trisubstituted derivatives of pyridine and acetonitrile under the same reaction conditions.

D. Preparation of *cis*-[(CH₃O)₃P]₃Mo(CO)₃, and related reactions. *cis*-[(CH₃O)₃P]₃Mo(CO)₃ has previously been prepared through displacement of cycloheptatriene from (C₇H₈)Mo(CO)₃.⁹ Direct reaction of (CH₃O)₃P and Mo(CO)₆ gives the *trans* isomer. The *cis* complex may be more inexpensively prepared as follows: a 1:4 mole ratio of (tmen)Mo(CO)₄ and (CH₃O)₃P were refluxed under nitrogen in dichloroethane for 35 minutes. The reaction mixture was filtered, the solvent removed *in vacuo* and the residue dissolved in a minimum amount of dichloroethane. An excess of *n*-hexane was then added to the solution, and the product was obtained as white crystals upon cooling over dry ice. A comparison of the infrared spectrum (hydrocarbon solvent) with that reported by Poilblanc and Bigorgne⁹ showed the complex to be spectroscopically pure. Reaction of (C₂H₅O)₃P, (*i*-C₃H₇O)₃P or (C₆H₅O)₃P with (tmen)Mo(CO)₄ under similar conditions yielded mixtures of the *cis*-di- and *cis*-tri-substituted phosphite derivatives. Solution spectra recorded during the progress of the reactions of (CH₃O)₃P, (C₂H₅O)₃P and (*i*-C₃H₇O)₃P indicated the presence of «mixed» derivatives of the type (phosphite)-(tmen)Mo(CO)₃ (see Table I) as determined through a comparison of their carbonyl stretching spectra to those of the analogous complexes in which dipy or phen was the bidentate ligand.³ The reaction of (C₆H₅)₃P with (tmen)Mo(CO)₄ gave the *trans*-disubstituted complex exclusively, with no evidence for the formation of a «mixed» derivative.

E. Preparation of *cis*-(C₆H₅)₃Sb(diphos)Mo(CO)₃, *cis*-(C₆H₁₁NH₂)(diphos)Mo(CO)₃, *cis*-(C₅H₅N)(diphos)Mo(CO)₃, and related reactions. (Diphos)Mo(CO)₄ and a fourfold excess of (C₆H₅)₃Sb were refluxed under nitrogen in xylene for 100 hours. The solution was filtered, the solvent removed *in vacuo*, and the residue extracted with hexane to remove unreacted (C₆H₅)₃Sb. The yellow [(C₆H₅)₃Sb](diphos)Mo(CO)₃ remained, and was dried *in vacuo*. *Anal.* Calc'd for C₄₇H₃₉O₃P₃SbMo: C, 60.60; H, 4.23. Found: C, 60.45; H, 4.33. (See Table I for the infrared spectra of derivatives reported in sections E, F and G). (Diphos)Mo(CO)₄ was refluxed under nitrogen in pyridine for 28 hours. The solution was filtered, the pyridine removed *in vacuo* and the residue recrystallized from acetone-water to give yellow (C₅H₅N)(diphos)Mo(CO)₃ which was dried *in vacuo*. *Anal.* Calc'd for C₃₄H₂₉N₃O₃P₂Mo: C, 62.00; H, 4.45. Found: C, 61.54; H, 4.66. (Diphos)Mo(CO)₄ was refluxed under nitrogen in cyclohexylamine for 23 hours; the work-up to yellow (C₆H₁₁NH₂)(diphos)Mo(CO)₃ was identical to that for (C₅H₅N)(diphos)Mo(CO)₃. *Anal.* Calc'd for C₃₅H₃₇N₃O₃P₂Mo: C, 61.94; H, 5.51. Found: C, 61.06; H, 5.36. (Diphos)Mo(CO)₄ was also refluxed in acetonitrile, and after 96 hours carbonyl stretching bands attributable to (CH₃CN)(diphos)Mo(CO)₃ were observed. However,

(7) G. R. Dobson, R. C. Taylor and T. D. Walsh, *Inorg. Chem.*, in press; NP = 1-(diethylamino)-2-(diphenylphosphino)ethane; NPN = bis(diethylaminoethyl)phenylphosphine.

(8) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961); diphos = 1,2-bis(diphenylphosphino)ethane.

(9) R. Poilblanc and M. Bigorgne, *Bull. Chim. Soc. France*, 1301 (1962).

Table I. Carbonyl Stretching Frequencies and Band Assignments for Some «Mixed» Derivatives of Mo(CO)₄

Complex	Symmetry*	Carbonyl Stretching Frequencies, Relative Intensities and Band Assignments**
<i>cis</i> -(C ₆ H ₁₁ NH ₂)(diphos)Mo(CO) ₃	C _s	1929 (s, A'); 1836 (s, A''); 1802 (s, A')
<i>cis</i> -(C ₅ H ₅ N)(diphos)Mo(CO) ₃	C _s	1931 (s, A'); 1840 (s, A''); 1814 (sh, A')
<i>cis</i> -(CH ₃ CN)(diphos)Mo(CO) ₃	C _s	^a 1931 (s, A'); 1836 (s, A''); 1817 (s, A')
<i>cis</i> -[(C ₆ H ₅) ₃ Sb](diphos)Mo(CO) ₃	C _{3v}	1948 (s, A ₁); 1857 (vs, E)
<i>trans</i> -[(C ₆ H ₅) ₃ P](diphos)Mo(CO) ₃	C _{2v}	1971 (w, A ₁); 1945 (m, A ₁); 1864 (vs, B ₁)
<i>trans</i> -[(C ₆ H ₅) ₃ As](diphos)Mo(CO) ₃	C _{2v}	1971 (w, A ₁); 1945 (m, A ₁); 1865 (vs, B ₁)
<i>trans</i> -[(C ₂ H ₅ O) ₃ P](diphos)Mo(CO) ₃	C _s	1978 (w, A'); 1950 (m, A'); 1875 (vs, A'')
<i>cis,cis</i> -[(C ₆ H ₅) ₃ P] ₂ (diphos)Mo(CO) ₂	C _{2v}	^b 1854 (s, A ₁); 1784 (s, B ₁)
<i>cis,cis</i> -[(C ₆ H ₅) ₃ As] ₂ (diphos)Mo(CO) ₂	C _{2v}	1851 (s, A ₁); 1784 (s, B ₁)
<i>cis,cis</i> -[(C ₂ H ₅ O) ₃ P] ₂ (diphos)Mo(CO) ₂	C _s	1874 (s, A); 1801 (s, A)
<i>cis</i> -[(CH ₃ O) ₃ P](tmen)Mo(CO) ₃	C _s	^b 1927 (s, A'); 1812 (s, A'); 1787 (s, A'')
<i>cis</i> -[(CH ₃ O) ₃ P](phen)Mo(CO) ₃	C _s	1931 (s, A'); 1838 (s, A'); 1795 (s, A'')
<i>cis</i> -[(C ₂ H ₅ O) ₃ P](tmen)Mo(CO) ₃	C _s	^b 1924 (s, A'); 1808 (s, A'); 1786 (s, A'')
<i>cis</i> -[(C ₂ H ₅ O) ₃ P](phen)Mo(CO) ₃	C _s	1928 (s, A'); 1831 (s, A'); 1791 (s, A'')
<i>cis</i> -[(<i>i</i> -C ₃ H ₇ O) ₃ P](tmen)Mo(CO) ₃	C _s	^b 1923 (s, A'); 1803 (s, A'); 1782 (s, A'')
<i>cis</i> -[(<i>i</i> -C ₃ H ₇ O) ₃ P](phen)Mo(CO) ₃	C _s	1925 (s, A'); 1825 (s, A'); 1787 (s, A'')

* Considering the bidentate and monodentate ligands as point charges, and differentiating between their bonding properties (diphos ~ (C₆H₅)₃P, (C₆H₅)₃As, (C₆H₅)₃Sb; ≠ C₆H₁₁NH₂, C₅H₅N, (C₂H₅O)₃P; tmen, phen ≠ (CH₃O)₃P, (C₂H₅O)₃P, (*i*-C₃H₇O)₃P). ** CHCl₃ solution unless otherwise noted; frequencies in cm⁻¹; band intensities: w: weak; m: medium; s: strong; v: very; sh: shoulder. ^a CH₃CN solution. ^b CH₂ClCH₂Cl solution.

due to the low reflux temperature, the pure product could not be obtained. Attempts to replace an additional carbonyl were also carried out. (Diphos)Mo(CO)₄ was refluxed for 144 hours with cyclohexylamine, 192 hours with pyridine, and 108 hours in dimethylformamide. The reaction mixtures, after work-up yielded a yellow powder which as found by chemical analysis and infrared spectrum to be (diphos)₂Mo(CO)₂. *Anal.* Calc'd for C₅₄H₄₈O₂P₄Mo: C, 68.38; H, 5.11; N, 0.00. Found: C, 68.28; H, 5.38; N, 0.00.

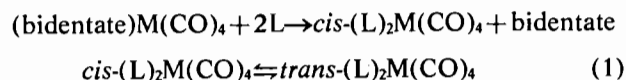
F. Preparation of *trans*-[(C₆H₅)₃P](diphos)Mo(CO)₃, and related reactions. (Diphos)Mo(CO)₄ and a four-fold excess of (C₆H₅)₃P were refluxed under nitrogen in xylene for 41 hours. The reaction mixture was filtered, the solvent removed *in vacuo*, the residue was taken up in chloroform, and was chromatographed on silica with ether-petroleum ether mixtures. Solvent was removed from the yellow fraction *in vacuo*, leaving *trans*-[(C₆H₅)₃P](diphos)Mo(CO)₃. *Anal.* Calc'd for C₄₇H₃₉O₃P₃Mo: C, 67.14; H, 4.69; P, 11.05. Found: C, 66.80; H, 5.10; P, 11.10. (Diphos)Mo(CO)₄ and an excess of (C₆H₅)₃As were refluxed under nitrogen in xylene for 41 hours. Bands attributable to *trans*-[(C₆H₅)₃As](diphos)Mo(CO)₃ were observed (Table I) but a satisfactory analysis for the product could not be obtained. Similarly, (diphos)Mo(CO)₄ and an excess of (C₂H₅O)₃P were refluxed under nitrogen for four hours in xylene, but the product could not be separated from excess (C₂H₅O)₃P.

G. Preparation of *cis*-[(C₆H₅)₃As]₂(diphos)Mo(CO)₂, *cis*-[(C₂H₅O)₃P]₂(diphos)Mo(CO)₂, and related reactions. (Diphos)Mo(CO)₄ and an excess of (C₆H₅)₃As were refluxed under nitrogen for 70 hours in xylene. The solution was filtered, the solvent removed *in vacuo*, and the excess (C₆H₅)₃As removed by extracting the residue with hexane. The yellow [(C₆H₅)₃As]₂(diphos)Mo(CO)₂ was then dried *in vacuo*. *Anal.* Calc'd for C₆₄H₅₄As₂O₂P₂Mo: C, 66.10; H, 4.69. Found: C, 66.21; H, 4.96. (Diphos)Mo(CO)₄ and an excess of (C₂H₅O)₃P were refluxed under nitrogen in xylene for 46 hours. The work-up of the product was

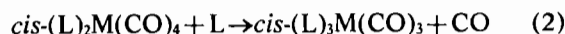
identical to that for [(C₆H₅)₃As]₂(diphos)Mo(CO)₂, the light yellow [(C₂H₅O)₃P]₂(diphos)Mo(CO)₂ being obtained by recrystallization from acetone-water. *Anal.* Calc'd for C₄₄H₅₄O₈P₄Mo: C, 54.35; H, 6.17. Found: C, 53.17; H, 5.81. (Diphos)Mo(CO)₄ and an excess of (C₆H₅)₃P were refluxed under nitrogen for 91 hours in mesitylene, but a satisfactory analysis of the product, shown by infrared spectrum to be either (diphos)₂Mo(CO)₂ or [(C₆H₅)₃P]₂(diphos)Mo(CO)₂ (probably the latter) could not be obtained.

Results and Discussion

A. Reactions, Stereochemistry and Spectra. For those (bidentate)M(CO)₄ complexes for which the initial reaction step involved the replacement of the bidentate ligand by a monodentate species (L), *i.e.*, (tmen)Cr(CO)₄, (NP)Cr(CO)₄, (NP)Mo(CO)₄, (DTH)Cr(CO)₄ and (DTH)Mo(CO)₄, the subsequent reaction path was found to be a function of the monodentate ligand employed. With the phosphine, phosphites and stibine investigated, no further replacement of carbonyls occurred in refluxing dichloroethane, although *trans-cis* isomerism of the disubstituted products was observed in several instances:

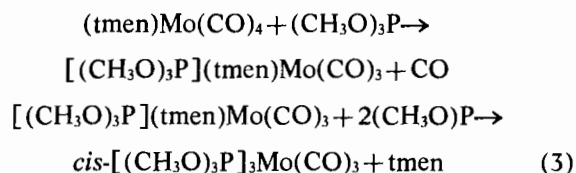


However, there was a rapid replacement of an additional carbonyl group to yield the *cis*-trisubstituted complexes with cyclohexylamine, pyridine or acetonitrile under the same reaction conditions:



In the (tmen)Mo(CO)₄ reactions, competing reaction paths are evident. For a ligand which is not sterically demanding *e.g.*, (CH₃O)₃P, the reaction proceeds to a

large degree through a «mixed» complex, followed by rapid replacement of the bidentate ligand, to give a *cis*-trisubstituted product:



These results are very similar to those observed by Angelici and Graham for the (dipy)Mo(CO)₄ system.^{4b}

Bulky groups such as (C₆H₅)₃P evidently inhibit the formation of a «mixed» complex, and the reaction path (1) is followed. With phosphites investigated, the reaction proceeds through both paths, the final concentrations of the di- and trisubstituted products being a measure of the extent to which the reaction proceeds through each (Figure 1). That the dependence of the

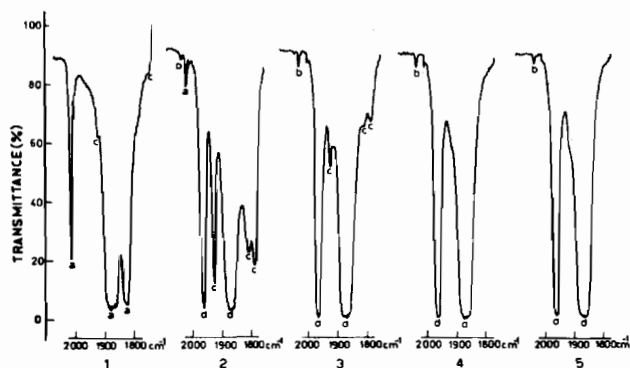
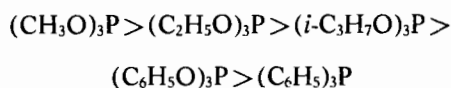


Figure 1. Solution spectra for reaction mixture of P(OCH₃)₃ + (tmen)Mo(CO)₄ in refluxing dichloroethane. Band attributable to (a), (tmen)Mo(CO)₄; (b), *cis*-[(CH₃O)₃P]₂Mo(CO)₄; (c), *cis*-[(CH₃O)₃P](tmen)Mo(CO)₃; (d), *cis*-[(CH₃O)₃P]₂Mo(CO)₃. See Table I, and equations (1) and (3). Cut 1, time = 0; 2, 15 minutes; 3, 30 minutes; 4, 45 minutes; 5, 360 minutes.

reaction path on the nature of the monodentate species is steric in nature is supported by the observed relative importance of the «mixed» derivative path for the various ligands investigated:



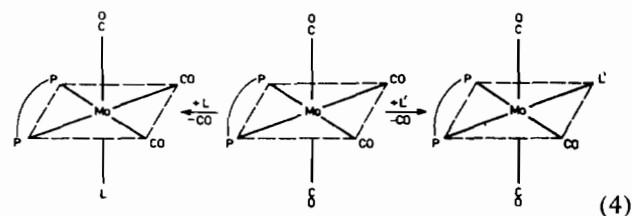
This order does not parallel the changing electronic nature of the P(III) ligands. Further, it has been observed that the bulky «mixed» tridentate ligand NPN,⁷ very similar sterically to tmen + (C₆H₅)₃P displaces only two carbonyls from Mo(CO)₆ to give (NPN)Mo(CO)₄.⁷ A comparison of (L)(tmen)Mo(CO)₃ and (L)(phen)Mo(CO)₃ carbonyl stretching frequencies (Table I) indicates that phen (and thus dipy) functions as a π-accepting ligand to an appreciable extent.

The preparation of the new complexes, *cis*-[(C₆H₅)₃Sb]₂Cr(CO)₄, *trans*-[(C₂H₅O)₃P]₂Cr(CO)₄, the spectral observation of the previously unreported *cis*-

{[(CH₃)₂N]₃P}₂Mo(CO)₄, and a convenient preparation of *cis*-[(CH₃O)P]₃Mo(CO)₃, which is not obtainable through direct reaction of the phosphite and Mo(CO)₆, underscore the potential usefulness of (bidentate)-M(CO)₄ species as intermediates to the preparation of other metal carbonyl derivatives. In this regard the lability of DTH is especially noteworthy; replacement of DTH by a monodentate ligand can be accomplished under very mild conditions (ca. 40°C).¹⁰

The reactions of (diphos)Mo(CO)₄ with monodentate Lewis base ligands may be compared to the previously reported reactions of (dipy)Mo(CO)₄ and (phen)Mo(CO)₄.^{3,4} The differences in the electronic and steric nature of the respective bidentate ligands may first be considered. Phen and dipy have been shown to be stabilizing ligands in these systems, CO replacement being easier in their tetracarbonyl derivatives than in Mo(CO)₆.⁴ Phosphines, on the other hand, are non-stabilizing,⁴ and further, diphos is considerably more sterically demanding than dipy or phen. That there should be differences in the ease of formation and stereochemistry of their mixed derivatives is therefore not surprising.

(Diphos)Mo(CO)₄ reacts with monodentate Lewis base ligands under drastic conditions (see Experimental Section) to give, depending upon the steric nature of the monodentate ligand either *cis* or *trans* trisubstituted mixed derivatives, as determined from infrared spectra and chemical analysis:



L = C₅H₅N, C₆H₁₁NH₂, CH₃CN, (C₆H₅)₃Sb

L' = (C₆H₅)₃P, (C₆H₅)₃As, (C₂H₅O)₃P

Ligand and carbonyl π-bonding effects are evidently of primary importance for Group VIb phosphine and phosphite complexes; it is therefore to be expected that a carbonyl group *trans* to another carbonyl will be more labile, and thus *cis* products are anticipated. The observed *trans* derivatives, the first such mixed derivatives to be prepared, may thus be attributed primarily to crowding at a face of the octahedron by the more sterically demanding L' ligands. It is of interest to note that while (C₆H₅)₃P and (C₆H₅)₃As give *trans* mixed derivatives, (C₆H₅)₃Sb gives the *cis* isomer. Evidently the larger size of the Sb atom reduces the steric interaction between the ligand phenyl groups and the metal carbonyl moiety.

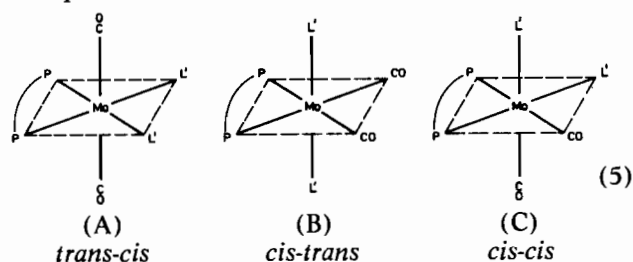
The infrared spectra for *cis*-complexes are similar to those reported for *cis*-(phen) and *cis*-(dipy) derivatives; where bonding properties of diphos and the monodentate ligand are similar, as in *cis*-[(C₆H₅)₃Sb](diphos)Mo(CO)₃ (see Table I) C_{3v} local symmetry of the carbonyl groups and two infrared-active bands (A₁ + E)

(10) Preliminary kinetic studies show the reactions of (DTH)M(CO)₄ (M=Cr, Mo) to obey a second order rate law, rate = k[(DTH)Mo(CO)₄][L]. G. C. Faber and G. R. Dobson, manuscript in preparation.

are expected and observed. As the bonding properties of diphos and the monodentate ligand diverge, C_s symmetry is applicable, and three carbonyl stretching bands ($2A' + A''$) are to be expected. Band assignments follow those of Cotton¹¹ from a consideration of the relative π -accepting abilities of diphos and the monodentate ligand.

Trans-trisubstituted derivatives are expected to exhibit C_{2v} local symmetry of the carbonyl groups for ligands which approach diphos in bonding properties. Three infrared-active carbonyl stretching modes ($2A_1 + B_1$) are to be expected, as are observed. The spectra are similar to those reported by Poilblanc and Bigorgne;⁹ their band assignments have been followed.

Under still more drastic conditions, for monodentate ligands (L') which have an appreciable ability to function as acceptors of metallic d_{π} electrons, an additional carbonyl group may be replaced to give mixed tetrasubstituted derivatives. The products can exist as three possible stereoisomers:



Since diphos and L' ligands generally are similar in bonding properties, as a first approximation infrared spectra again may be interpreted on the basis of the local symmetry of the carbonyl groups undisplaced from the octahedron. It thus may be expected that (5A) would exhibit approximate D_{4h} symmetry, for which one infrared-active carbonyl stretching mode (E_u) would be expected. The fact that the observed spectra show two bands of approximately equal intensity split by some 65 cm^{-1} is a strong argument against (5A). Further, since these complexes are derived from *trans*-trisubstituted derivatives, it may be expected that a carbonyl *trans* to the more strongly π -accepting ligand, CO, will be most readily replaced.

Both (5B) and (5C) should be expected to exhibit approximate C_{2v} local symmetry of the carbonyl groups, and thus a choice cannot be made between them on the basis of carbonyl stretching spectra. The steric demands of the bonded ligands, however, might favor a dissociative mechanism, and, if the stereochemistry of the intermediate is maintained, (C) would be the expected isomer. Both (B) and (C) would appear to be equally probable on the basis of steric requirements. If indeed the complexes exhibit *cis-cis* stereochemistry, they are the first mixed derivatives of this type, although, of course, there are many known complexes of the type *cis*-(bidentate)₂M(CO)₂.

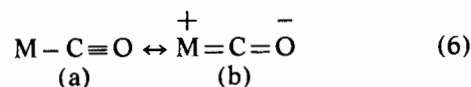
No tetrasubstituted mixed derivative of phen or dipy containing monodentate ligands which have only a limited ability (or none) to enter into metal-ligand «back bonding» could be synthesized.³ The same observation may be made with regard to tetrasubstitution products of (diphos)Mo(CO)₄. Under very drastic conditions

the only isolable product of the attempted reaction of (diphos)Mo(CO)₄ with cyclohexylamine, pyridine or dimethylformamide was (diphos)₂Mo(CO)₂. The significance of this observation will be discussed in a later section.

B. Bonding Implications. The most striking feature of the results reported here is the ability of amines, and ligands of similar bonding properties to labilize carbonyl groups. In reactions in which the bidentate ligand initially is displaced, more highly substituted derivatives are obtained for such ligands than for phosphines or phosphites under the same reaction conditions. For reactions of (tmen)Mo(CO)₄, a path involving initial replacement of a carbonyl by a phosphite leads ultimately to a *cis* trisubstituted phosphite derivative, whereas with initial replacement of tmen, only disubstituted phosphite complexes are obtained. Finally, reactions of (diphos)Mo(CO)₄ proceed only under drastic conditions, whereas for (phen)Mo(CO)₄ or (dipy)Mo(CO)₄, reaction conditions are much milder.³ Thus, for example, the preparation of *cis*-[(C₆H₅)₃Sb](bidentate)Mo(CO)₃ complexes in refluxing xylene requires 100 hours for diphos, but only two hours for phen.³ The possibility that the rigorous conditions required for (diphos)Mo(CO)₄ reactions may at least in part be due to the stringent steric requirements of the diphos ligand cannot, however, be dismissed; kinetic investigations of the reactions of (diphos)Mo(CO)₄ are presently under way in this laboratory.

The labilizing influence of amines and ligands of similar bonding properties was first discussed by Angelici and Graham⁴ for reactions of (dipy)M(CO)₄ complexes. These workers correlated the «hardness»¹² of the substituent with the lability of CO, and also pointed to the same effect in a variety of octahedral manganese carbonyl complexes. It was further noted that all such reactions for which kinetic data were available proceed, at least in part, through a dissociative mechanism in which the rate-determining step is envisioned to involve breaking of a metal-carbon bond.

The labilizing influence of «hard» bases (in terms of bonding in metal carbonyls, those ligands which are relatively good σ -donors, and relatively poor π -acceptors) may be attributed to either destabilization of the ground state or to stabilization of the transition state; the former would involve weakening of the metal-carbon bond by the «hard» base. In terms of metal-carbonyl bond strengths as are commonly inferred from carbonyl stretching frequencies or force constants,¹³ ground state destabilization is not to be expected in carbonyl derivatives of «hard» bases. Hard base ligands, being relatively poor π -acceptors, yield relatively low carbonyl stretching frequencies compared to analogous derivatives containing non-labilizing «soft» basic ligands (relatively good π -acceptors) such as phosphines and phosphites. The oft-invoked valence bond description of bonding in metal carbonyls,



(12) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(13) G. R. Dobson, I. W. Stolz and R. K. Shelton, *Adv. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

(11) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

would suggest a strengthening of metal-carbon bonds, *i.e.*, a greater contribution of (6b) to a resonance description of bonding with lowered carbonyl stretching frequencies, as are observed for «hard» base derivatives. This conclusion, together with the observed lack of correlation between labilizing ability and ligand basicity led Angelici and Graham to suggest that the observed labilizing influence of «hard» bases was primarily the result of their stabilization of the transition state.

To ascertain whether or not M-C bonds in derivatives of hard bases are in fact strengthened as C-O bonds are weakened, infrared spectra in the M-C stretching region (500-300 cm^{-1}) for the (bidentate)Mo(CO)₄ complexes investigated were obtained (Table II). Surprisingly,

in octahedral complexes do not mix appreciably and thus differences in ligand-metal bond strengths will have only a limited influence on carbonyl stretching frequencies. However, since the strength of M-C bonds is dependent upon both σ and π contributions, and yet only the π part is strongly reflected in the carbonyl stretching frequencies of octahedral complexes, the possibility exists that lowered carbonyl stretching frequencies need not indicate stronger metal-carbon bonds. To the contrary, the infrared data suggest that a strongly σ donating ligand may substantially decrease the Lewis acidity of a metal toward CO, inhibiting carbon-metal σ bonding. For amines and similar «hard» bases, the decrease in carbon-metal σ bond strength evidently is greater than the increase in M-CO π bond

Table II. Metal-Carbon and Carbon-Oxygen Stretching Frequencies for Some *cis*-L₂Mo(CO)₄ Molecules*

Complex	ν_{MC} (cm^{-1})**	ν_{CO} (cm^{-1})**
(tmen)Mo(CO) ₄	410 (w); 398 (vw); 374 (sh); 364 (vs)	2013, 1890, 1875, 1837 ^b (CHCl ₃)
(phen)Mo(CO) ₄	409 (w); 394 (sh); 379 (sh); 368 (vs)	2025, 1906, 1875, 1826 ^a (CHCl ₃)
(DTH)Mo(CO) ₄	405 (w); 395 (sh); 375 (vs)	2030, 1919, 1905, 1869 ^b (CHCl ₃)
(NP)Mo(CO) ₄	433 (s); 428 (sh); 392 (m); 383 (s)	2019, 1905, 1893, 1849 ^b (CHCl ₃)
[(C ₂ H ₅) ₂ P] ₂ Mo(CO) ₄	428 (m); 413 (m); 404 (m); 392 (s) ^b	2014, 1915, 1901, 1890 ^b (hydrocarbon)
(diphos)Mo(CO) ₄	430 (ms); 418 (sh); 402 (w); 387 (m)	2028, 1932, 1919, 1906 (hydrocarbon)

* Spectra in the 600-250 cm^{-1} region have also been obtained for (bidentate)Cr(CO)₄ complexes. Although definitive M-C band assignments for these complexes cannot be made at present, they permit more definitive assignments for (bidentate)Mo(CO)₄ M-C stretching bands to be made on the basis of the observed differences in M-C stretching frequencies for Cr(CO)₆ and Mo(CO)₆ (L. H. Jones, *Spectrochim. Acta*, 19, 329 (1963)). ** All MC stretching data taken for CsI pellets, except for [(C₂H₅)₂P]₂Mo(CO)₄, the spectrum of which was recorded in hydrocarbon solvent. CO stretching spectra obtained in solvent given in parentheses. ^aE. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

these frequencies show a rough *decrease*, rather than the expected increase, as the corresponding carbonyl stretching frequencies decrease.¹⁴ Moreover, the decreases are substantial, when compared to the frequency of the vibration involved. Thus these data suggest that as carbonyl bond strengths are decreased in going from derivatives of «soft» to «hard» bases, there is also a concomitant decrease in metal-carbon bond strength. The apparent anomaly may be explained through a consideration of both σ and π bonding effects in these complexes.

The effects of changes in carbon-metal σ -bonding and metal-carbonyl $d_{\pi}-p_{\pi}$ * «back bonding» on carbonyl stretching frequencies have previously been discussed.¹⁵ Upon coordination of CO, carbonyl stretching frequencies are raised, but the effect is small; the primary effect comes from π -bonding, with frequencies and force constants decreasing as metallic charge is accepted by the carbonyl ligands. Moreover, in the «symmetry factorability» approximation,¹⁶ σ and π metallic orbitals

strength due to the replacement of carbonyl groups by ligands of poorer π -accepting ability; the M-C bond is thus weakened. It would thus seem that the labilizing ability of «hard» bases is at least in part due to this effect.

At this point Angelici and Graham's other objection⁴ to the ground state destabilization explanation for the labilizing effects of «hard» bases, *viz.*, the lack of correlation between ligand basicities and ligand labilizing abilities will be considered; it was observed that some phosphine and phosphite «soft» base ligands are more basic than certain amines, and yet are not labilizing ligands. That this observation should be significant rests on the premise that the pK_a of a phosphine or amine also describes its basicity toward an octahedral metal carbonyl moiety.

For the latter, however, the steric factors may be quite significant. There have been no octahedral metal carbonyl complexes reported of primary phosphines, undoubtedly because of their limited stability to air; the tertiary phosphines which have been investigated generally are bulky. On the other hand, most «hard» bases which have been investigated are primary amines and other similar ligands which would be expected to exert relatively little steric influence. The steric factors thus well may dictate poorer overlap for «soft» base

(14) Although coupling of δ_{MCO} and ν_{CO} may be expected to be extensive, differences in coupling effects may be minimized among derivatives of the same stereochemistry. Unlike CO bonds, MC bonds are insulated from environmental effects (although, of course, MCO deformations are not), and thus pellet spectra should be fairly reliable. For example, MC stretching frequencies for Mo(CO)₆ differ by only 1 cm^{-1} from gas phase to mull (L. H. Jones, *Spectrochim. Acta*, 19, 329 (1963)).

(15) G. R. Dobson, *Inorg. Chem.*, 4, 1673 (1965).

(16) Although it has been shown that the «symmetry factorability» approximation (F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 85, 4432 (1962)) is not strictly valid (S. F. A. Kettle, *Inorg. Chem.*, 4, 1661 (1965); *J. Chem. Soc., A*, 420 (1966)), and the carbonyl stretching frequencies for two derivatives have been interpreted on the basis of its inapplicability,³ there is also a large body of experimental data which shows it to be a reasonable one. For example, Poilblanc⁶ has obtained

results which show that inductive effects of R groups bonded to amines in (amine)Mo(CO)₄ complexes are not reflected in carbonyl stretching frequencies. Thus it would appear that the approximation has validity; the extent to which it is valid is open to question.

ligands, with a corresponding decrease in the basicity observed toward the octahedral metal carbonyl moiety. Several examples of the importance of steric, rather than basicity factors in these systems can be cited. For example, ligand basicities vary diethylamine > triethylamine > cyclohexylamine, and yet diethylamine and cyclohexylamine form (amine)(phen)Mo(CO)₃ complexes, while the bulkier triethylamine does not.³ A similar steric effect has been reported for the diamines; (N,N,N',N'-tetraethylethylenediamine)Mo(CO)₄ decomposes even *in vacuo*, while (ethylenediamine)Mo(CO)₄ is air stable even though the bulkier N,N,N',N'-tetraethylethylenediamine is more basic. Further, as previously mentioned, the second amine group in the sterically demanding ligand NPN fails to coordinate; the observed product is (NPN)Mo(CO)₄.⁷ Thus it is not unreasonable that steric effects may substantially affect the basicity of a ligand in these systems; a lack of correlation between ligand basicity and labilizing ability is not surprising.

If indeed σ bonding effects are of importance in octahedral metal carbonyl systems, expectations based upon their consideration must be wholly consistent with observed data. Three areas of interest will be considered in turn: (a) observed product stereochemistry; (b) bond lengths; and (c) observed limits to the number of carbonyls which can be replaced by π -accepting or non- π -accepting ligands.

(a) *Observed Product Stereochemistry.* The observed product stereochemistry for octahedral metal carbonyl complexes of «hard» bases may qualitatively be explained in terms of both σ and π bonding influences as follows: a «hard» base strongly decreases the Lewis acidity of the metal, and thus decreases the metal-carbon bond strength of each carbonyl; the relatively poor π -accepting ability of a «hard» base ligand, however, increases M-C π bond strength more strongly at the carbonyl *trans* to the ligand than at the *cis* positions. Thus *cis* carbonyls are expected to be more labile, in agreement with the *cis*-directing influence of «hard» bases.¹³

(b) *Bond Lengths.* It has recently been noted¹⁷ that Cr-C bond lengths in (benzene)Cr(CO)₃ and (diethylenetriamine)Cr(CO)₃ are essentially equal despite the marked differences in carbonyl stretching frequencies for the two complexes (for (benzene)Cr(CO)₃, hydrocarbon solvent, $\nu_{\text{CO}} = 1987, 1917$; for (diethylenetriamine)Cr(CO)₃, solvent not reported, $\nu_{\text{CO}} = 1895, 1759$ cm.⁻¹).^{18,11} The frequencies would imply, in the valence bond view, a greater contribution from VIb to a resonance description of the bonding, and thus a shorter M-C bond length for the latter. In the absence of evidence for differences in Cr-C σ bonding, the equality of bond lengths was taken to indicate that Cr-C-O bonding in the two complexes was similar – that neither benzene nor diethylenetriamine functioned as a π -acceptor. The marked differences in carbonyl stretching frequencies were ignored. It would seem

more reasonable to attribute higher carbonyl stretching frequencies in (benzene)Cr(CO)₃ to the ability of benzene to function as a π -acceptor, and the nearly equal Cr-C bond lengths to the inhibition of C-Cr σ bonding by the strongly basic diethylenetriamine.

(c) *Observed Limits to Carbonyl Replacement by Ligands.* For reactions of (diphos)Mo(CO)₄ it is observed that an additional carbonyl can be replaced, but only by ligands which have a substantial ability to function as π -acceptors. For reactions of cyclohexylamine, dimethylformamide and pyridine the observed product was found to be (diphos)₂Mo(CO)₂. Similar observations have been made with regard to reactions of (phen)Mo(CO)₄ and (dipy)Mo(CO)₄: tetrasubstituted products were observed only for strongly π -accepting ligands.³ The failure of a fourth «hard» base ligand to coordinate in these systems, in which it is evident that a fourth metal-carbon bond can be broken, is inexplicable in terms of π -bonding alone, or through the argument that «hard» bases somehow stabilize the transition state from which the product is formed. It is explicable, however, in terms of drastic reduction in Lewis acidity of the metal through successive replacement of carbonyls by strongly σ -donating ligands. The formation of tetrasubstituted derivatives of phosphines and phosphites may be attributed to ligand-metal bond stabilization by strongly π -accepting ligands.

The observed limits of carbonyl replacement by various polydentate ligands may also be mentioned in this regard. Whereas only three carbonyls can be replaced by non- π -bonding amine ligands, dipy and phen can replace all six. On the other hand, diphos replaces only four, even though zerovalent (diphos)₃M can be prepared directly.¹³ These results are inexplicable in terms of π -bonding alone, but are readily understandable in terms of both σ and π -bonding. Amines, while strongly labilizing are unable to function as π -acceptors; the formation of a fourth metal-amine bond is strongly inhibited by the charge on the metal resulting from the formation of the first three. Dipy and phen are also strongly labilizing, but the heterocyclic ring systems can stabilize ligand-metal bonds through $d_{\pi}-p_{\pi}^*$ «back bonding». Phosphines are non-labilizing (relatively poor σ -donors) and thus metal-carbon bonds, strengthened by increased metal-carbonyl «back bonding» are not readily broken in (diphos)₂M(CO)₂.

Thus there is a body of evidence which indicates that differences in σ -bonding in octahedral metal carbonyls may be of importance; it is at least clear that σ -bonding effects should no longer be ignored.

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(17) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 5, 1851 (1966).

(18) R. D. Fischer, *Chem. Ber.*, 93, 165 (1960).