fellowship from the A. P. Sloan Foundation and a Teacher-Scholar Grant from the Camille and Henry Dreyfus Foundation.

Registry No. $Cp_2Rh_2(NO)_2$, 67426-08-8; $Cp_3Rh_3(NO)_2$, 75495-01-1; $Cp_2Rh_2(NO)(NO_2)$, 75365-54-7; $[Rh(CO)_2Cl]_2$, 14523-22-9; $CpRh(CO)_2$, 12192-97-1; $Cp_3Rh_3(CO)_3$, 12148-54-8.

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Mixed-Metal Carbonyl Complexes of Cr, Mo, and W Containing Bridging $Ph_2PCH_2CH_2PPh_2$

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Received May 30, 1980

Numerous carbonyl complexes of Cr, Mo, and W are known which contain $Ph_2PCH_2CH_2PPh_2$, L–L, as a chelating ligand. Less common are those in which L–L serves as a bridging ligand, particularly between atoms of two different metals.[2,3] Our recent successes in the syntheses of complexes containing L–L as a monodentate ligand (e.g., $(OC)_5WL{-}L$ and $(OC)_4W(L{-}L)_2$) by base and free-radical catalyzed addition reactions prompted us to explore these approaches as avenues to mixed-metal L–L-bridged complexes.[4]

Experimental Section

Physical Measurements. ^{31}P NMR and infrared spectra were obtained from chloroform solutions as described elsewhere.[4] Chemical shifts downfield from H_3PO_4 are measured as positive. Microanalyses were obtained from Galbraith Laboratories, Knoxville, Tenn.

Materials. Diphenylvinylphosphine, diphenylphosphine, and the metal carbonyls were purchased from Pressure Chemical Co. and used without further purification. All reactions were carried out under a nitrogen atmosphere.

$(OC)_5WPPh_2CH{=}CH_2$ and $(OC)_5WPPh_2H$ were prepared as described previously.[4] $(OC)_5CrPPh_2CH{=}CH_2$ (38.2%) and $(OC)_5WPPh_2H$ (95%)[5,6] were prepared by the indirect method of Strohmeier.[4] $(OC)_5MoPPh_2CH{=}CH_2$ (97%) and $(OC)_5MoPPh_2H$ (73%)[5,6] were prepared from the thermal reaction of phosphine and $Mo(CO)_6$ in 1,2-dimethoxyethane.[7]

$(OC)_5CrPPh_2CH{=}CH_2$: mp 58–59 °C; IR 1985 (B_1), 2067 ($A_1^{(2)}$), 1943 ($E + A_1^{(1)}$); ^{31}P NMR δ 47.4.

Anal. Calcd for $C_{19}H_{13}O_5PCr$: C, 56.45; H, 3.24; P, 7.66. Found: C, 56.33; H, 3.31; P, 7.72.

$(OC)_5MoPPh_2CH{=}CH_2$: mp 57–58 °C; IR 1991 (B_1), 2074 ($A_1^{(2)}$), 1949 ($E + A_1^{(1)}$); ^{31}P NMR δ 29.3.

Anal. Calcd for $C_{19}H_{13}O_5PMo$: C, 50.91; H, 2.92; P, 6.91. Found: C, 50.87; H, 3.07; P, 7.06.

$(OC)_5CrPPh_2H$: mp 60–61 °C (lit.[4] mp 55–65 °C); ^{31}P NMR δ 32.9.

$(OC)_5MoPPh_2H$: mp 74–75.5 °C (lit.[4] mp 73–75 °C); ^{31}P NMR δ 6.7.

Base-Catalyzed Reactions of $(OC)_5MPPh_2H$ with $(OC)_5M'PPh_2CH{=}CH_2$ (M = Cr, Mo, W). The same experimental procedure was used to prepare each of the six dimetallic complexes. The procedure will be illustrated for the molybdenum–tungsten complex. To a solution of $(OC)_5WPPh_2H$ (4.22 mmol) in dry THF (80 ml) were added $(OC)_5MoPPh_2CH{=}CH_2$ (4.22 mmol) and potassium *tert*-butoxide (0.08 g). The solution was heated under reflux for 1 h, cooled, and stripped of solvent; the resulting residue was crystallized from a CH_2Cl_2/CH_3OH mixture to give $(OC)_5MoPPh_2CH_2CH_2PPh_2W(CO)_5$ in 88% yield.

$(OC)_5MoPPh_2CH_2CH_2PPh_2W(CO)_5$: mp 195–198 °C dec; IR 1986 (B_1), 2074 ($A_1^{(2)}$), 1948 ($E + A_1^{(1)}$); ^{31}P NMR δ_{MoP} 31.6 ($^2J_{PP}$ = 35.5 Hz), δ_{WP} 12.9 ($^2J_{PP}$ = 35.5, J_{WP} = 241.6 Hz).

Anal. Calcd for $C_{36}H_{24}O_{10}P_2MoW$: C, 45.12; H, 2.52; P, 6.46. Found: C, 44.99; H, 2.62; P, 6.76.

$(OC)_5MoPPh_2CH_2CH_2PPh_2Cr(CO)_5$: mp 190–191 °C dec; IR 1987 (B_1), 2075, 2065 ($A_1^{(2)}$), 1950 ($E + A_1^{(1)}$); ^{31}P NMR δ_{MoP} 31.8 ($^2J_{PP}$ = 32.4 Hz), δ_{CrP} 51.1 ($^2J_{PP}$ = 32.4 Hz).

$(OC)_5MoPPh_2CH_2CH_2PPh_2Mo(CO)_5$: mp 198–200 °C dec (lit.[3] 192–194 °C); IR 1992 (B_1), 2075 ($A_1^{(2)}$), 1954 ($E + A_1^{(1)}$); ^{31}P NMR δ_P 31.7.

$(OC)_5WPPh_2CH_2CH_2PPh_2Cr(CO)_5$: mp 205–208 °C dec; IR 1986 (B_1), 2067, 2077 ($A_1^{(2)}$), 1944 ($E + A_1^{(1)}$); ^{31}P NMR δ_{WP} 13.0 ($^2J_{PP}$ = 32.2, J_{WP} = 241.5 Hz), δ_{CrP} 50.9 ($^2J_{PP}$ = 32.2 Hz).

Anal. Calcd for $C_{36}H_{24}O_{10}P_2CrW$: C, 47.29; H, 2.65; P, 6.78. Found: C, 46.93; H, 2.78; P, 6.85.

$(OC)_5WPPh_2CH_2CH_2PPh_2W(CO)_5$: mp 217–218 °C dec;[2] IR 1984 (B_1), 2073 ($A_1^{(2)}$), 1943 ($E + A_1^{(1)}$); ^{31}P NMR δ_{WP} 12.7 (m, ABX pattern, $^2J_{PP}$ = 36.6 Hz, J_{WP} = 241.6 Hz).

$(OC)_5CrPPh_2CH_2CH_2PPh_2Cr(CO)_5$: mp 192–193 °C dec (lit.[3] 200–201 °C); IR 1986 (B_1), 2065 ($A_1^{(2)}$), 1945 ($E + A_1^{(1)}$); ^{31}P NMR δ_P 51.1.

Results and Discussion

There are six possible $(OC)_5ML{-}LM'(CO)_5$ complexes of Cr, Mo, and W, three homometallic ($M = M'$) and three heterometallic ($M \neq M'$). Of these only the homometallic complexes have been previously reported.[2,3]

Substitution reactions provide a straightforward method of synthesis for the homometallic species. For example, L–L displaces Y from $(OC)_5MY$ under mild conditions (eq 1)[2,8]

$$2(OC)_5MY + L{-}L \rightarrow (OC)_5ML{-}LM(CO)_5 + 2Y \qquad (1)$$

$$Y = C_6H_5NH_2,\ I^-$$

The mixed-metal complexes, however, cannot be obtained directly in good yield from such reactions because of competitive formation of the more symmetrical ($M = M'$) products. The $M \neq M'$ complexes could be prepared by isolating $(OC)_5ML{-}L$, a complex containing L–L as a monodentate ligand, and allowing it to react with $(OC)_5M'Y$.

We have now shown that the isolation of the intermediate "dangling" ligand complex may be avoided entirely by using starting materials which all contain coordinated phosphines (eq 2). The reactants are easily synthesized, and the six

$$(OC)_5MPPh_2CH{=}CH_2 + (OC)_5M'PPh_2H \xrightarrow{KO(t\text{-}Bu)} (OC)_5MPPh_2CH_2CH_2PPh_2M'(CO)_5 \qquad (2)$$

$$M = Cr,\ Mo,\ W \text{ and } M' = Cr,\ Mo,\ W$$

dimetallic combinations of Cr, Mo, and W are obtained in good yield when the reaction is carried out in the presence of catalytic amounts of potassium *tert*-butoxide.[9] Either combination of reactants gives the desired product. For example, the synthesis of $(OC)_5CrL{-}LW(CO)_5$ proceeds equally well

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[9] The free-radical catalyst AIBN does not appear to be useful in these reactions. Reactions with this catalyst led to the formation of blue decomposition products, and only starting materials were isolated.

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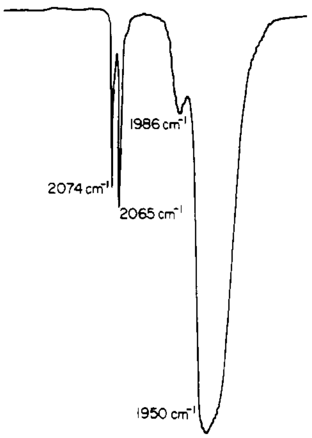

Figure 1. Carbonyl region of the infrared spectrum of $(OC)_5CrPPh_2CH_2CH_2PPh_2Mo(CO)_5$.

with $(OC)_5WPPh_2CH{=}CH_2$ and $(OC)_5CrPPh_2H$ or with $(OC)_5CrPPh_2CH{=}CH_2$ and $(OC)_5WPPh_2H$ as starting materials. The method should be very useful for preparing a variety of bis(tertiary phosphine)-bridged complexes.

The carbonyl regions of the infrared spectra of the three symmetrical complexes $(OC)_5WL{-}LW(CO)_5$, $(OC)_5MoL{-}LMo(CO)_5$, and $(OC)_5CrL{-}LCr(CO)_5$ show bands expected for pentacarbonyl moieties of C_{4v} symmetry. The E and $A_1^{(1)}$ modes overlap as is often observed for monosubstituted group 6 carbonyl complexes.[10] The mixed-metal complex $(OC)_5MoL{-}LW(CO)_5$ gives rise to a spectrum in which molybdenum carbonyl absorptions cannot be distinguished from those of the tungsten carbonyls. Since the $A_1^{(1)}$ modes of $(OC)_5W{-}L{-}LW(CO)_5$ and $(OC)_5MoL{-}LMo(CO)_5$ absorb at 2073 and 2075 cm^{-1}, respectively, resolution of these individual absorptions in $(OC)_5MoL{-}LW(CO)_5$ would not be expected. For both $(OC)_5CrL{-}LMo(CO)_5$ and $(OC)_5CrL{-}LW(CO)_5$, however, resolution of the two $A_1^{(1)}$ modes is achieved, consistent with the difference of approximately 9 cm^{-1} between the $A_1^{(1)}$ absorption for $(OC)_5CrL{-}LCr(CO)_5$ and that of either the analogous molybdenum or tungsten complex (Figure 1). The overlapping E modes were not resolved for any of the mixed-metal complexes.

The ^{31}P NMR spectra of the mixed-metal complexes show chemical shifts downfield from phosphoric acid in the order Cr > Mo > W as has been observed for simpler systems.[10] The two different phosphorus environments give rise to splitting due to phosphorus–phosphorus coupling. In addition tungsten-183–phosphorus-31 coupling is observed in the spectra of the tungsten complexes.

The ^{31}P NMR spectrum of $(OC)_5WL{-}LW(CO)_5$ is of special interest (Figure 2). The 14.28% abundant tungsten-183 is distributed such that the $(OC)_5{}^{183}WL{-}L^{183}W(CO)_5$, $(OC)_5{}^{183}WL{-}LW(CO)_5$, and $(OC)_5WL{-}LW(CO)_5$ distribution is 2.03, 24.48, and 73.48%, respectively. The satellite pattern observed in Figure 2 arises from $(OC)_5{}^{183}WL{-}LW(CO)_5$. This molecule, which contains two nonequivalent phosphorus nuclei as a result of the tungsten-183 isotope, gives rise to an ABX spectrum. The AB portion of the spectrum consists of two ab subspectra indicated by lines 1, 2, 4, and 6 and by lines 3, 5, 7, and 8. The recently reported NMR analysis of $Ph_2P(^{77}Se)CHCHP(Se)Ph_2$ parallels that for the tungsten complex exactly.[11] The value of $^1J_{WP}$ extracted from this spectrum is 241.6 Hz which is the same as was observed directly in the spectra of the two mixed dimetallic tungsten complexes. Within the limit of measurement (±0.2 Hz), the value for $^4J_{WP}$ is zero.

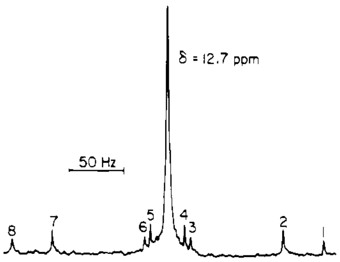

Figure 2. ^{31}P NMR spectrum of $(OC)_5WPPh_2CH_2CH_2PPh_2W(CO)_5$.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $(OC)_5MoPPh_2CH_2CH_2PPh_2W(CO)_5$, 75365-60-5; $(OC)_5MoPPh_2CH_2CH_2PPh_2Cr(CO)_5$, 75365-61-6; $(OC)_5MoPPh_2CH_2CH_2PPh_2Mo(CO)_5$, 14489-09-9; $(OC)_5WPPh_2CH_2CH_2PPh_2Cr(CO)_5$, 75365-62-7; $(OC)_5WPPh_2CH_2CH_2PPh_2W(CO)_5$, 15413-06-6; $(OC)_5CrPPh_2CH_2CH_2PPh_2Cr(CO)_5$, 15024-28-9; $(OC)_5WPPh_2CH{=}CH_2$, 64012-10-8; $(OC)_5CrPPh_2CH{=}CH_2$, 72868-75-8; $(OC)_5MoPPh_2CH{=}CH_2$, 75365-63-8; $(OC)_5CrPPh_2H$, 18399-60-5; $(OC)_5MoPPh_2H$, 18399-61-6; $(OC)_5WPPh_2H$, 18399-62-7.

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Convenient Preparation and Isolation of Pure Potassium Cyclopentadienyldicarbonylferrate, K[(η^5-C_5H_5)Fe(CO)$_2$]

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Received April 7, 1980

Recently developed procedures for the cleavage of metal carbonyl dimers circumvent the need for hazardous, cumbersome reducing agents such as sodium amalgam[1,2] or sodium potassium alloy.[3] Potassium hydride[4] and certain trialkylborohydrides[5] efficiently reduce $[Mn(CO)_5]_2$, $[Co(CO)_4]_2$, and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in THF solution at room temperature to afford $Mn(CO)_5^-$, $Co(CO)_4^-$, and $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ in nearly quantitative yield. However, when either of these reagents is employed for the cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$, sluggish reaction rates are encountered unless a highly coordinating cosolvent such as hexamethylphosphoramide is used with THF. A sodium dispersion in THF serves as a cleavage reagent which has been employed for the in situ preparation of derivatives of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$.[13] Since complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]R$[6] (where R = allyl, alkyl) can promote a variety of useful transformations in organic molecules, it is of interest to develop a convenient technique for cleaving $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ which will also yield an isolable salt that can later be used as a stoichiometric reagent under a variety of conditions.

We find that potassium benzophenone ketyl rapidly and cleanly reduces $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in THF at room tem-

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