molybdenum (D) was prepared similarly. The $^{31}$P($^1$H) NMR spectrum of D consists of a singlet at $\delta$ 18.5.

A suspension of Ligand and trimethylphosphine (0.18 mL, 0.0018 mol) in diethyl ether (25 mL) was added to a solution of tetrakis(acetato)dimolybdenum (0.38 g, 0.0009 mol) and trimethylphosphine (0.18 mL, 0.0018 mol) in diethyl ether (25 mL) at 0°C. After the solution was stirred for 5 h (0°C), the diethyl ether was removed under vacuum from the purple suspension. Pentane (50 mL) was added to the residue which was filtered, and the filtrate was evaporated to ca. 10 mL and cooled (-10°C). The red prisms (0.24 g, 40%) were collected and dried under vacuum.

Bis(pivalato)bis[(trimethylsilyl)methylamido](trithiophosphine)dimolybdenum(II) (F). Bis(pivalato)bis[(trimethylsilyl)methylamido]bis(trithiophosphine)dimolybdenum, 73622-35-2; bis(triethylphosphine)dimolybdenum, 73622-34-1; lithium bis(dimethylsilyl)amide, 4039-32-1; lithium bis(trimethylsilyl)amide, 4039-32-1; lithium (triethylphosphine)dimolybdenum, 1023-105-6; tetrakis(acetato)dimolybdenum, 13622-36-3; J, 13622-37-4; K, 13622-38-5; L, 13622-39-6; M, 13728-25-3; tetraakis(pivalato)dimolybdenum, 73622-38-5; lithium (triethylphosphine)dimolybdenum, 73622-39-6; M, 73728-24-2; N, 73728-23-1; O, 73728-25-3; tetraakis(acetato)dimolybdenum, 142209-12-7; tris(pivalato)dimolybdenum, 73622-39-6; M, 73728-24-2; N, 73728-23-1; O, 73728-25-3; tetrakis(acetato)dimolybdenum, 142209-12-7; lithium bis(dimethylsilyl)amide, 4039-32-1; lithium (triethylphosphine)dimolybdenum, 10568-44-2; bis(triethylphosphine)dimolybdenum, 73612-22-3.

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Registry No. A, 73622-29-4; B, 73622-30-7; C, 73622-31-8; D, 73622-32-9; E, 73622-33-0; F, 73622-34-1; G, 73622-35-2; H, 73622-36-3; I, 73622-37-4; K, 73622-38-5; L, 73622-39-6; M, 73728-24-2; N, 73728-23-1; O, 73728-25-3; tetraakis(acetato)dimolybdenum, 142209-12-7; tris(pivalato)dimolybdenum, 36608-07-8; tetrakis(pivalato)dimolybdenum, 55946-68-4; lithium bis(dimethylsilyl)amide, 4039-32-1; lithium (triethylphosphine)dimolybdenum, 10568-44-2; bis(triethylphosphine)dimolybdenum, 73612-22-3.

Notes

Contributions from the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Parc Valrose, 06034 Nice, France.

Derivatives of (γ5-Cyclopentadienyl)molybdenum
Tricarbonyl Hydride and Chloride, γ5-C5H5Mo(CO)3X (X = H, Cl), Containing a Bicyclic Phosphorus–Nitrogen Ligand

Joachim Wachter, François Jeanneaux, and Jean G. Riess*

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Substitution reactions of γ5-C5H5Mo(CO)3X (X = H, Cl) with bidentate group 5a ligands in 1:1 molar ratio have been well investigated only for X = Cl. In this case, derivatives of two types have been obtained, depending on whether only carbon monoxide is displaced or the chloride ion as well; ionic products are formed in the latter case. Bis(phosphine) ligands have been found to give both neutral and ionic compounds,2 with the most π-accepting ones, such as (F3P)2NCH2, leading to the substitution of CO only.2c In contrast, the bidentate ligands which have little or no back-bonding capacity such as bipyrindines and pyridine Schiff bases have resulted only in cationic products.2a,3

The combination of a π-accepting center with a σ-donating site is now realized in the tautomeric open form B of the bicyclopentaphosphorane (C5H5)2HP(OCH2CH2)2N, 1.4 We wish to report that in its reaction with C5H5Mo(CO)3Cl, I exhibits

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all the combinations of behaviors described above, whereas it shows only restricted reactivity toward C,H,Mo(CO)3H.

Experimental Section

Elemental analyses and mass spectra were performed by the Centre de Microanalyse du CNRS. They are shown together with physical properties and infrared data in Table I. All procedures were carried out under nitrogen. All solvents were freshly distilled under nitrogen from appropriate drying agents. The phosphorane (C,H,)HPQ,HzCH2N, (abbreviated phoran), and the other starting materials C,H,Mo(CO)3X (X = H, Cl) were prepared according to published procedures.

Preparations. C,H,Mo(CO)2(phoran)H, 2. A mixture of 0.49 g (2 mmol) of C,H,Mo(CO)3H with 0.42 g (2 mmol) of phosphorane 1 and 60 mL of tetrahydrofuran was magnetically stirred at room temperature for 1 h. After evaporation of the solvent the oily residue was extracted with two portions of 50 mL of ether. Evaporation of the ether and washing twice with 50 mL of pentane gave 0.35 g (yield 41%) of an orange-red powder. This compound could be converted into 3 by stirring 0.15 g (0.60 mmol) of 2 in 30 mL of chloroform at 30 °C for 4 h. After evaporation of the solvent, the sample was washed with 30 mL of ether and 50 mL of pentane. The residue consisted of 0.05 g (yield 18%) of an orange powder. Anal. Calcd for C,H,Mo(CO)2(phoran)Cl: C, 44.03; H, 4.13; Cl, 7.65. Found: C, 42.15; H, 3.98; Cl, 7.37. S(31P) 185 (CDC13).

C,H,Mo(CO)(phoran)Cl, 3. A 0.56-g (2 mmol) sample of C,H,Mo(CO)3Cl and 0.42 g (2 mmol) of phosphorane 1 were dissolved in 100 mL of ether. The solution was magnetically stirred at room temperature for 20 h. The precipitate was filtered and washed with ether to give 0.76 g (yield 82%) of orange 2. The product is soluble in benzene as well as in ethanol and can be recrystallized from CHCl3/Et2O, 2:1. Molar conductance (10⁻³ m in acetone): 5.7 Ω⁻¹ cm² mol⁻¹.

C,H,Mo(CO)(phoran)Cl, 4. The solution of 0.46 g (1 mmol) of C,H,Mo(CO)(phoran)Cl, 3, in 100 mL of benzene was boiled under reflux for 2 h. The solution was cooled to room temperature, and the precipitate formed was filtered to give 0.26 g (yield 60%) of fine red crystals of 4. The product is insoluble in benzene, ether, and ethanol and sparingly soluble in chloroform. [C,H,Mo(CO)(phoran)]PF₆, 5. A 1.85-g (4 mmol) sample of C,H,Mo(CO)(phoran)Cl, 3, was dissolved in 95 mL of ethanol while being heated to 60 °C (bath temperature). After filtration, 70 mL of water and 0.9 g (5.5 mmol) of NH₄PF₆ were added. The solution was magnetically stirred until the first fine precipitate appeared (between 30 and 40 min). To complete precipitation, a further addition of NH₄PF₆ (0.5 g, 3 mmol), dissolved in 100 mL of water, was made. After the solution was stirred for 4 h, the salt was filtered and carefully washed with water and ether. The yield was 1.8 g (79%) of a brown-yellow powder of 5. Crystallization from 1:1 acetone-ether gave dark yellow needles. Molar conductance (10⁻³ m in acetone): 122.5 Ω⁻¹ cm² mol⁻¹.

Results and Discussion

Stirring of a THF solution of C,H,Mo(CO)3H with the bicyclic phosphorane 1 at room temperature results in the substitution of only one CO group. Thus the infrared spectra of the resulting compound 2 exhibit two CO absorptions and a ν(NH) frequency at 3380 cm⁻¹, characteristic of the uncoordinated nitrogen atom. As 2 belongs to the class of square-pyramidal cyclopentadienyl dicarbonyl complexes with facile cis/trans exchange, its ¹H and ³¹P NMR spectra in CDCl₃ solutions give at room temperature a singlet for C,H₃H₃.

Notes
Notes

Table II. Proton, Phosphorus, and Carbon NMR Data for Compounds 2–5

<table>
<thead>
<tr>
<th>compd</th>
<th>CH$<em>2$N (J$</em>{P-C}$)</th>
<th>CH$<em>2$O (J$</em>{P-C}$)</th>
<th>C$_5$H$<em>5$ (J$</em>{P-C}$)</th>
<th>C$_5$H$<em>4$ (J$</em>{P-C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpMo(CO)$_3$(phoran)H, 2</td>
<td>m3.44, m3.96</td>
<td>m$^\dagger$3.26 (&lt;0.2)$^e$</td>
<td>d m6.41 (65.1)$^e$</td>
<td>d m6.41 (12.2)$^e$</td>
</tr>
<tr>
<td>CpMo(CO)$_3$(phoran)Cl, 3</td>
<td>m3.44, m4.01</td>
<td>m$^\dagger$3.26 (&lt;0.2)$^e$</td>
<td>d m6.41 (65.1)$^e$</td>
<td>d m6.41 (12.2)$^e$</td>
</tr>
<tr>
<td>CpMo(CO)$_3$(phoran)H, 4</td>
<td>m3.38, m4.12</td>
<td>m$^\dagger$3.26 (&lt;0.2)$^e$</td>
<td>d m6.41 (65.1)$^e$</td>
<td>d m6.41 (12.2)$^e$</td>
</tr>
</tbody>
</table>

Scheme I

\[
\begin{align*}
\text{Cp} & \equiv \text{cyclopentadienyl} \\
\text{b} & \text{The NMR spectra were recorded at 90, 36, 45, and 22.63 MHz for } ^1H, ^31P, \text{and } ^13C, \text{respectively, on a Bruker WH-90 DS spectrometer; broad-band decoupled for } ^31P \text{ and } ^13C. \text{ Chemical shifts are given in ppm downfield from } Me_3Si (\text{internal}) \text{ and } 85\% \text{ H}_{2}PO_4 (\text{external}), \text{ coupling constants in Hz.} \\
\text{c} & \text{singlet, } d = \text{doublet, } sp = \text{septet, } s = \text{multiplet.} \\
\text{d} & \text{not observed.} \\
\text{f} & \text{cis isomer.} \\
\text{g} & \text{trans isomer.} \\
\end{align*}
\]

a Cp = Cp$_7$H$_5$C$_6$(R) = OCH$_3$, C$_6$H$_5$_3 derivatives. The trans isomer is characterized by a doublet for the cyclopentadienyl protons at 5.14 ppm with a coupling constant $^31P$-H of 2.5 Hz and a $^31P$ resonance signal at 202 ppm. The cis/trans ratio was estimated by means of the C$_5$H$_5$ proton resonances as 94.6: (DCI$_3$, 25 °C). Separation of the isomers by column chromatography could not be realized because of their too strong absorption on SiO$_2$ and Al$_2$O$_3$. The high $\nu$(NH) infrared frequency of 3355 cm$^{-1}$ confirms that the nitrogen is not coordinated. The conductometric results further exclude an ionic structure containing a chelate ligand bonded by nitrogen and phosphorus. However, one observes weak singlets at 5.75 ppm for the C$_5$H$_5$ protons and at 205 ppm for the phosphorus atom in the NMR spectra of 3, prepared by both methods; these could be explained by the presence of small amounts of [(C$_5$H$_5$)$_2$(CO)$_2$Mo(phoran)]$^+$PF$_6$.

In contrast to our expectations, a cationic product could not be obtained directly. We suppose it is formed as an intermediate when 3 is dissolved in a mixture of ethanol and water. The initial step could consist of a weakening of the Mo=Cl bond under the influence of the polar solvent or an equilibrium of cis 3 with the chloride salt in solution, which would be influenced by precipitation of the ionic compound. In fact, the addition of an excess of NH$_4$PF$_6$ provokes the cationic chelate complex 5 to precipitate. Its analytical and spectroscopic data are in agreement with the proposed structure. The $\nu$(NH) and $\nu$(CO) infrared frequencies are increased by the positive charge on the metal atom. The $^31P$ NMR spectrum contains one singlet for the coordinated phosphorus and one septet for the PF$_6^-$ anion. The $^1H$ NMR spectrum shows one singlet for the cyclopentadienyl protons, whereas the diastereotopic ligand protons are as broad as in the compounds described above. In contrast, the $^13C$ NMR spectra show that the two cycles of the ligand have different orientations with respect to the cyclopentadienyl ring. Thus the phosphorane carbon atoms of 5 give four well-separated doublets, whereas in the monocoordinated 3 they appear only as three doublets. The other chemical shifts are consistent with data obtained from other $^13C$-H$_2$Mo(CO)$_3$X derivatives.

Boiling of 3 in benzene results in the substitution of a second CO group to give product 4. Because of the initial cis configuration in the starting material the same arrangement

---


should exist for chlorine and phosphorus in the monocarbonyl compound. The presence of only one isomer is confirmed by the NMR spectra. Due to coordination to the metal the \(\nu (\text{NH})\) frequency has decreased to 3160 cm\(^{-1}\). In spite of the easy migration of the N-H proton in 1, we did not observe the evolution of hydrogen chloride in the re- actions of \(\text{C}_2\text{H}_5\text{Mo(CO)}_2\text{Cl}\) even in the presence of pyridine.

In summary, the reaction of \((\eta^2-\text{C}_2\text{H}_4\text{Mo(CO)}_3\text{Cl})\text{H}\) in THF with the bicyclophosphorane 1 (abbreviated phoran) gives \(\text{C}_2\text{H}_5\text{Mo(CO)}_2\text{Cl}(\text{phoran})\text{H}, 2\), which slowly converts in \(\text{CHCl}_3\) solution to \(\text{C}_2\text{H}_5\text{Mo(CO)}_2\text{Cl}(\text{phoran})\text{Cl}, 3\). The same product can also be obtained from \(\eta^2-\text{C}_2\text{H}_4\text{Mo(CO)}_2\text{Cl}\) and 1 in diethyl ether. Although a cationic form \([\text{C}_2\text{H}_5\text{Mo(CO)}_2\text{Cl}(\text{phoran})]\text{Cl}\) of 3 may exist in traces, 3 can be converted in good yields into the \([\text{C}_2\text{H}_5\text{Mo(CO)}_2\text{Cl}(\text{phoran})]\text{PF}_5\) salt (5) by addition of \(\text{NH}_2\text{PF}_6\) in aqueous ethanol. Reflux of 3 in benzene results in a further substitution of CO to give \(\text{C}_2\text{H}_5\text{Mo(CO)}(\text{phoran})\text{Cl}\), 4. The ligand is monodentate and phosphorus-bound in 2 and 3 and bidentate in 4 and 5, as shown in the \(^1\text{H}, \^13\text{C}, \text{and } \^31\text{P NMR.}\)

Acknowledgment. We thank Dr. Bernard Seppe for measuring the NMR spectra.

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Chemical and X-ray Structural Properties of Bis(bis(diphenylphosphino)methane)rhodium(1) Tetrafluoroborate


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Recent studies on the catalytic properties of metal complexes with chelating diphosphine ligands have shown rather large rate and selectivity effects as a function of the diphosphine chelate ring size. 3,5 Specific studies have involved hydroformylation using a platinum-diphosphine-tin system, 3,5 hydrogenation using a rhodium chloride-diphosphine system, 6,7 and carbonylation of aldehydes using a cationic bis(diphenylphosphino)rhodium system. 6,7 In these cases where diphosphines of the type \(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\) with \(n=1-6\) were used, the catalytic rates showed maxima for values of \(n\) ranging from 3 to 5. Clearly a combination of chelate ring strain, flexibility, and electronic bonding properties is important.

During our studies on the catalytic decarbonylation of aldehydes using \(\text{Rh}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]^{2+}\) complexes with \(n=1-6\), it became apparent that the value of \(n\) played a major role in determining reactivity and selectivity. 5,6 In this reaction the lability of CO from the intermediate \(\text{Rh}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]^{2+}\text{CO}^{-}\) is important and in some cases may be the rate-determining step. 5,6 Therefore, we set out to characterize these carbonyl complexes for \(n=1\) (dppm), 3 (dppp), and 4 (dpbb). The \(n=2\) (dppe) analogue cannot be prepared whereas the dppm and dppp complexes are readily formed at 25 °C in solution by reaction of CO gas with bis(diphosphine)rhodium tetrafluoroborate. This reaction is reversible. The reaction of CO with \(\text{Rh(dpbb)}^{2+}\) leads to dimeric products \(\text{Rh}_2(\text{dpbb})_2(\text{CO})_x\) with \(x = 2, 3,\) and 4. The characterization and structural properties of the dpbb complexes will be published elsewhere. 9 The chemical and \(^{31}\text{P NMR properties of Rh(dpdpm),CO}^+\) and \(\text{Rh(dpmp),CO}^+\) and the single-crystal X-ray structure of the former are presented here. The solid-state structure of \([\text{Rh(dpdpm)}\text{CO}]\text{BF}_4\) is only the second crystallographic example of dpdpm chelating to a single Rh atom. 10

Experimental Section

\(^{31}\text{P}[\text{H}]\) NMR spectra were recorded at 40.5 MHz by using a Varian Associates XL-100 FT instrument, and chemical shifts are referenced to external standard 85% \(\text{H}_2\text{PO}_4\) with positive shifts in parts per million upfield. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer. Hydrated rhodium(II) chloride was obtained on loan from Matthey Blish, Inc., and bis(diphenylphosphino)methane (dppm) and 1,3-bis(diphenylphosphino)propane (dpbb) were purchased from Strem Chemicals.

Synthesis of Compounds. \([\text{Rh(dpdpm)}\text{CO}]\text{BF}_4\), \(\text{Rh}_2\text{Cl}_2(\text{COD})_2(\text{COD}=1,5\text{cyclooctadiene})\) 11 (140 mg, 0.57 mmol) was stirred in 25 mL of acetone under a purified \(\text{N}_2\) atmosphere. Upon addition of \(\text{AgBF}_4\) (128 mg, 0.66 mmol) to this slurry, the rhodium complex dissolved, and a white precipitate formed, leaving a pale yellow solution. This solution was refluxed for 30 min and filtered. The filtrate was added to a toluene solution (30 mL) of \(\text{dpdpm (438 mg, 1.14 mmol)},\) giving an orange color. Slow evaporation of the acetone yielded orange-red crystals. All the above manipulations were carried out under a \(\text{N}_2\) atmosphere by using standard Schlenk techniques. The compound is air sensitive and may be recrystallized from dichloromethane-diethyl ether. Anal. Calcld for \(\text{RhC}_9\text{H}_{14}\text{OP}_4\text{BF}_4:\) C, 62.65; H, 4.59. Found: C, 62.95; H, 4.55. \(^{31}\text{P}[\text{H}]\) NMR (25 °C, acetone-\(\text{d}_6\)): \(\delta = 23.2,\) (d, \(J_{\text{Rh-P}} = 116\) Hz).

\([\text{Rh(dpdpm)}\text{CO}]\text{BF}_4\). Gaseous CO was bubbled through a dichloromethane solution of \([\text{Rh(dpdpm)}\text{CO}]\text{BF}_4\), for ca. 15 min. The color changed from orange to yellow after ca. 5 min. Gold crystals were obtained upon the addition of diethyl ether under a CO atmosphere. IR (KBr disk): \(\nu (\text{CO}) 1945\) cm\(^{-1}\). Anal. Calcld for \(\text{RhC}_9\text{H}_{14}\text{OP}_4\text{BF}_4:\) C, 62.09; H, 4.46. Found: C, 61.79; H, 4.67. \(^{31}\text{P}[\text{H}]\) NMR (25 °C, acetone-\(\text{d}_6\)): \(\delta = 22.5,\) (d, \(J_{\text{Rh-P}} = 98\) Hz).

\([\text{Rh(dpmm)}\text{CO}]\text{BF}_4\) was prepared in a manner analogous to that for the dppm complex from \([\text{Rh(dpdpm)}\text{CO}]\text{BF}_4\). IR (KBr disk): \(\nu (\text{CO}) 1945\) cm\(^{-1}\). Anal. Calcld for \(\text{RhC}_9\text{H}_{14}\text{OP}_4\text{BF}_4:\) C, 62.57; H, 4.99. Found: C, 62.98; H, 5.44. \(^{31}\text{P}[\text{H}]\) NMR (80 °C, acetone-\(\text{d}_6\)): \(\delta = 14.27,\) and 13.28 (\(A_{2B_2X}\)_X pattern, \(J_{\text{P-P}} = 86\) and 113 Hz, \(J_{\text{P-BF}} = 45\) Hz, in good agreement with the literature values). 3

X-ray Structure Determination. A crystal of \([\text{Rh(dpdpm)}\text{CO}]\text{BF}_4\) was fastened to the end of a thin glass fiber with 5-min epoxy resin. The dimensions of this rectangular crystal were \(0.25 \times 0.20 \times 0.20\) mm. The crystal was found to be monoclinic by the automatic peak searching, centering, and indexing routines of the Enraf-Nonius SDP-CAD 4 system. 12 A Delaunay reduction calculation (program TRACER) 12 did not indicate a higher symmetry, and the monoclinic crystal class was verified by examination of the intensities of numerous reflections required to be equivalent by the \(2/m\) crystal symmetry. The space group \(P2_1/c\) was chosen due to the systematic absences in the data (\(h0l, \(l=2n+1\), and \(0k0, \(k=2n+1\)) and was used to solve the structure (using SHELX 76) (space group \(P2_1/c\)). The unit cell dimensions were determined by least-squares refinement of the angular values of 25 Mo K\(\alpha\) peaks centered on a CAD 4 diffractometer and are \(a = 11.281 (2)\), \(b = 10.0020-1669/80/1319-2172$01.00/0 © 1980 American Chemical Society