20 mL, and cooling (−10 °C) gave red *prisms* in 45% (0.33 g) yield. Bis(acetato)bis[bis(trimethylsilyl)amido]bis(triethylphosphine)dimolybdenum (D) was prepared similarly. The $^{31}P\{^1H\}$ NMR spectrum of D consists of a singlet at δ 18.5.

Bis(acetato)bis[(trimethylsilyl)methylamido]bis(trimethylphosphine)dimolybdenum(II) (E). Lithium (trimethylsilyl)methylamide (0.29 g, 0.0027 mol) in diethyl ether (25 mL) was added to a suspension of tetrakis(acetato)dimolybdenum (0.38 g, 0.000 90 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]bis(trimethylphosphine)dimolybdenum(II) (F). To tetrakis(pivalato)dimolybdenum (0.29 g, 0.000 49 mol) dissolved in diethyl ether (25 mL) was added trimethylphosphine (0.10 mL, 0.0015 mol) at 0 °C. Lithium (trimethylsilyl)methylamide (0.16 g, 0.0015 mol) in diethyl ether (25 mL) was added and stirred at 0 °C for 8 h. The diethyl ether was removed from the blue-red suspension under vacuum. The residue was extracted with pentane (50 mL) and filtered, and the filtrate was concentrated to ca. 5 mL and cooled to −10 °C. The red *prisms* were collected and dried under vacuum. The yield was 0.29 g (80%). Bis(pivalato)bis[(trimethylsilyl)methylamido]bis(triethylphosphine)dimolybdenum(II) (G) was prepared similarly. The $^{31}P\{^1H\}$ NMR spectrum of G yielded a singlet at δ 20.2.

Bis(acetato)bis[bis(dimethylsilyl)amido]bis(dimethylphenylphosphine)dimolybdenum(II) (I). Lithium bis(dimethylsilyl)amide (0.26 g, 0.0019 mol) in diethyl ether (25 mL) was added to a suspension of tetrakis(acetato)dimolybdenum (0.40 g, 0.000 93 mol) and dimethylphenylphosphine (0.27 mL, 0.0019 mol) in diethyl ether (25 mL) at 0 °C. After the solution was stirred at 0 °C for 12 h, the diethyl ether was removed under vacuum. The residue was extracted with pentane (100 mL) and filtered. The filtrate was concentrated to ca. 90 mL and cooled (−10 °C). The red *prisms* were collected and dried under vacuum. The yield was 0.16 g (20%). Bis(acetato)bis[bis(dimethylsilyl)amido]bis(trimethylphosphine)dimolybdenum(II) (H) was prepared similarly.

Bis(pivalato)bis[bis(dimethylsilyl)amido]bis(trimethylphosphine)dimolybdenum(II) (J). To tetrakis(pivalato)dimolybdenum (0.26 g, 0.000 44 mol) in diethyl ether (25 mL) at 0 °C were added trimethylphosphine (0.09 mL, 0.000 87 mol) and lithium bis(dimethylsilyl)amide–0.58-diethyl ether complex (0.16 g, 0.000 87 mol) in diethyl ether (25 mL). After the solution was stirred for 4 h (0 °C), the diethyl ether was removed under vacuum. The residue was extracted with pentane (100 mL) and filtered, and the filtrate was concentrated to ca. 70 mL and cooled (−10 °C). The red *prisms* were collected and dried under vacuum. The yield was 0.28 g (80%). Bis(pivalato)bis[bis(dimethylsilyl)amido]bis(triethylphosphine)dimolybdenum(II) (L) was prepared similarly. The latter complex yielded a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.4.

Tris(pivalato)[bis(trimethylsilyl)amido](trimethylphosphine)dimolybdenum(II) (M). Lithium bis(trimethylsilyl)amide (0.20 g, 0.0012 mol) in toluene (25 mL) was added to a solution of tetrakis(pivalato)dimolybdenum (0.36 g, 0.000 60 mol) and trimethylphosphine (0.12 mL, 0.0012 mol) in toluene (25 mL) at room temperature. After the solution was stirred for 8 h, the toluene was removed under vacuum, and the residue was extracted with pentane (50 mL). After filtration, the filtrate was concentrated to ca. 20 mL and cooled (−10 °C). The orange *prisms* were collected and dried under vacuum. The yield was 0.24 g (55%). Tris(pivalato)[bis(trimethylsilyl)amido](triethylphosphine)dimolybdenum(II) (N) was prepared similarly. The $^{31}P\{^1H\}$ NMR spectrum of N consisted of a singlet at δ 18.2.

Tris(pivalato)[bis(trimethylsilyl)amido](dimethylphenylphosphine)dimolybdenum(II) (O). Lithium bis(trimethylsilyl)amide–1.46-diethyl ether complex (0.41 g, 0.0014 mol) in toluene (25 mL) was added to a solution of tetrakis(pivalato)dimolybenum (0.42 g, 0.000 70 mol) and dimethylphenylphosphine (0.20 mL, 0.0014 mol) in toluene (25 mL). The red suspension was stirred for 7 h. The toluene was removed under vacuum, and the residue was exposed to vacuum for 8 h. The residue was extracted with pentane (35 mL) and filtered, and the filtrate was concentrated to ca. 20 mL and cooled (−10 °C). The red crystals were collected and were dissolved with pentane (50 mL) and filtered, the filtrate was concentrated to ca. 15 mL, and cooling (−10 °C) yielded red *prisms* (0.28 g, 54%).

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Registry No. A, 73622-29-4; B, 73622-30-7; C, 73622-31-8; D, 73622-32-9; E, 73651-42-0; F, 73622-33-0; G, 73622-34-1; H, 73622-35-2; I, 73622-36-3; J, 73622-37-4; K, 73622-38-5; L, 73622-39-6; M, 73728-24-2; N, 73728-23-1; O, 73728-25-3; tetrakis(acetato)dimolybdenum, 14221-06-8; tetrakis(trifluoroacetato)dimolybdenum, 36608-07-8; tetrakis(pivalato)dimolybdenum, 55946-68-4; lithium bis(trimethylsilyl)amide, 4039-32-1; lithium (trimethylsilyl)methylamide, 10568-44-2; lithium bis(dimethylsilyl)amide, 73612-22-3.

Notes

Contribution from the Laboratoire de Chimie Minérale
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Derivatives of (η^5-Cyclopentadienyl)molybdenum Tricarbonyl Hydride and Chloride, η^5-$C_5H_5Mo(CO)_3X$ (X = H, Cl), Containing a Bicyclic Phosphorus-Nitrogen Ligand

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Substitution reactions of η^5-$C_5H_5Mo(CO)_3X$ (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 $(F_2P)_2NCH_3$, leading to the substitution of CO only.[2c] In contrast, the bidentate ligands which have little or no back-bonding capacity such as bipyridines 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 bicyclophosphorane $(C_6H_5)HP(OCH_2CH_2)_2N$, **1**.[4] We wish to report that in its reaction with $C_5H_5Mo(CO)_3Cl$, **1** exhibits

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[2] (a) P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organomet. Chem.*, **7**, 449 (1967); (b) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 94 (1967); (c) R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2396 (1978); (d) P. W. Lednor, W. Beck, H. G. Fick, and H. Zippel, *Chem. Ber.*, **111**, 615 (1978).

[3] H. Brunner and W. A. Herrmann, *Chem. Ber.*, **105**, 3600 (1972).

[4] (a) D. Bondoux, I. Tkatchenko, D. Houalla, R. Wolf, C. Pradat, J. G. Riess, and B. F. Mentzen, *J. Chem. Soc., Chem. Commun.*, 1023 (1978); (b) C. Pradat, J. G. Riess, D. Bondoux, B. F. Mentzen, I. Tkatchenko, and D. Houalla, *J. Am. Chem. Soc.*, **101**, 2234 (1979).

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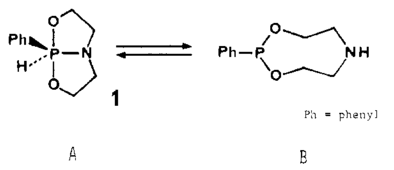

all the combinations of behaviors described above, whereas it shows only restricted reactivity toward $C_5H_5Mo(CO)_3H$.

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 $(C_6H_5)HP(OCH_2CH_2)_2N$, **1** (abbreviated phoran),[5] and the other starting materials $C_5H_5Mo(CO)_3X$ (X = H, Cl)[6] were prepared according to published procedures.

Preparations. $C_5H_5Mo(CO)_2$(phoran)H, 2. A mixture of 0.49 g (2 mmol) of $C_5H_5Mo(CO)_3H$ 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 $C_5H_5Mo(CO)_2$(phoran)Cl: C, 44.03; H, 4.13; Cl, 7.65. Found: C, 42.15; H, 3.98; Cl, 7.37. $\delta(^{31}P)$ 185 ($CDCl_3$).

$C_5H_5Mo(CO)_2$(phoran)Cl, 3. A 0.56-g (2-mmol) sample of $C_5H_5Mo(CO)_3Cl$ 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 $CHCl_3/Et_2O$, 2:1. Molar conductance (10^{-3} m in acetone): 5.7 Ω^{-1} cm^2 mol^{-1}.

$C_5H_5Mo(CO)$(phoran)Cl, 4. The solution of 0.46 g (1 mmol) of $C_5H_5Mo(CO)_2$(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.

[$C_5H_5Mo(CO)_2$(phoran)]PF_6, 5. A 1.85-g (4-mmol) sample of $C_5H_5Mo(CO)_2$(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 NH_4PF_6 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 NH_4PF_6 (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} cm^2 mol^{-1}.

Results and Discussion

Stirring of a THF solution of $C_5H_5Mo(CO)_3H$ 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 noncoordinated nitrogen atom. As **2** belongs to the class of square-pyramidal cyclopentadienyl dicarbonyl complexes with facile cis/trans exchange,[7] its ^1H and ^{31}P NMR spectra in CD_2Cl_2 solutions give at room temperature a singlet for C_5H_5,

Table I. Properties of Compounds 2–5

			anal.														infrared,[e] cm^{-1}		
			mol wt		% C		% H		% N		% Cl		% P		% Mo				
compd[a]	color	mp,[b] °C	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found	ν(NH)	ν(CO)	ν(PF_6)
CpMo(CO)$_2$(phoran)H, 2	orange-red	89 dec	429	431[c]	47.56	47.32	4.70	4.73	3.26	3.13			7.22	7.14	22.35	20.96	3380 w, m	1945, 1860 vs	
CpMo(CO)$_2$(phoran)Cl, 3	brick red	151 dec	463	437[c]	44.03	44.07	4.13	4.18	3.02	2.97	7.65	7.31	6.68	6.72	20.69	20.37	3355 w	1966, 1880 vs	
CpMo(CO)(phoran)Cl, 4	red	186 dec	435	437[c]	44.10	43.19	4.40	4.42	3.21	3.14	8.14	7.82	7.11	6.83	22.02	21.39	3160 m	1800 vs	
[CpMo(CO)$_2$(phoran)] PF$_6$, 5	dark yellow	194 dec	573	571[d]	35.62	35.06	3.34	3.32	2.44	2.41			10.81	10.72	16.74	16.69	3300 m	1990, 1900 vs	843 vs

[a] Cp = η^5-cyclopentadienyl. [b] Uncorrected. [c] Determination by 70-eV mass spectroscopy (related to ^{98}Mo). The highest mass for 3 is $[M - CO]^+ = 437$. [d] Determination by vapor pressure osmometry in acetone solution. [e] The infrared spectra were determined in KBr disks.

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(5) D. Houalla, T. Mouheich, M. Sanchez, and R. Wolf, *Phosphorus*, **5**, 229 (1975).

(6) (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); (b) E. O. Fischer, *Inorg. Synth.*, **7**, 136 (1963).

(7) K. W. Barnett and D. W. Slocum, *J. Organomet. Chem.*, **44**, 1 (1972).

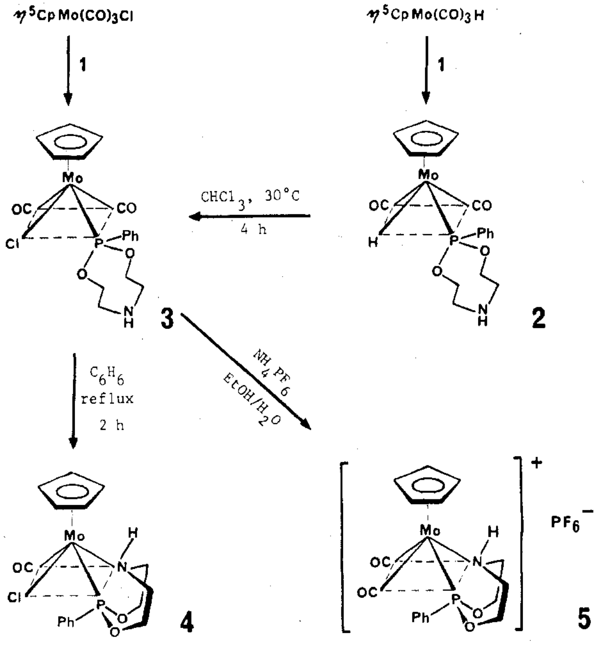
Table II. Proton, Phosphorus, and Carbon NMR Data for Compounds **2–5**

	$\delta(^1H)^{b,c}$						$\delta(^{31}P)^{b,c}$		
compd^a	CH_2N	CH_2O	C_5H_5 (J_{P-H})	N–H	C_6H_5	M–H (J_{P-H})	P–Mo	PF_6 (J_{P-F})	solvent (*t*, °C)
$CpMo(CO)_2$(phoran)H, **2**	$^{m}3.44$	$^{m}3.96$	$^{s}5.26$ (<0.2),^{e} $^{s}5.13$ (<0.2)^f	*d*	$^{m}7.49$	$^{d}-6.41$ (65.1),^{e} $^{d}-6.23$ (23.2)^f	$^{s}200$,^{e} $^{s}210^f$		CD_2Cl_2 (−60)
$CpMo(CO)_2$(phoran)Cl, **3**	$^{m}3.44$	$^{m}4.01$	$^{s}5.29$ (<0.2)	*d*	$^{m}7.50$		$^{s}185$		$CDCl_3$ (25)
CpMo(CO)(phoran)Cl, **4**	$^{m}3.38$	$^{m}4.41$	$^{d}5.06$ (2.6)	$^{m}5.72$	$^{m}7.48$		$^{s}194$		$CDCl_3$ (25)
[$CpMo(CO)_2$(phoran)] PF_6, **5**	$^{m}3.21$	$^{m}3.96$, $^{m}4.64$	$^{s}6.0$ (<0.2)	$^{m}7.42$	$^{m}7.70$		$^{s}198$	$^{sp}-145$ (708)	acetone-d_6 (25)

	$\delta(^{13}C)^{b,c}$					
compd^a	CH_2N (J_{P-C})	CH_2O (J_{P-C})	C_5H_5	C_6H_5 (J_{P-C})	CO (J_{P-C})	solvent (25 °C)
$CpMo(CO)_2$(phoran)Cl, **3**	$^{d}48.9$ (5)	$^{d}67.6$, $^{d}68.5$ (7)	$^{s}94.9$	$^{m}128.2$–131.0, $^{d}140.5$ (59)	$^{d}240.0$ (5), $^{d}254.7$ (37)	$CDCl_3$, 0.06 m $Cr(acac)_3$
[$CpMo(CO)_2$(phoran)] PF_6, **5**	$^{d}50.1$, $^{d}55.9$ (6)	$^{d}64.02$, $^{s}68.4$ (5)	$^{s}96.2$	$^{m}129.1$–130.1, $^{s}133.3$	*d*	acetone-d_6

^{a} Cp = η^5cyclopentadienyl. ^{b} The NMR spectra were recorded at 90, 36, 45, and 22.63 MHz for ^1H, ^{31}P, and ^{13}C, respectively, on a Bruker WH-90 DS spectrometer; broad-band decoupled for ^{31}P and ^{13}C. Chemical shifts are given in ppm downfield from Me_4Si (internal) and 85% H_3PO_4 (external), coupling constants in Hz. ^{c} s = singlet, d = doublet, sp = septet, m = multiplet. ^{d} Not observed. ^{e} Cis isomer. ^{f} Trans isomer.

Scheme I



a doublet for H–M, and a singlet for phosphorus. These signals split at −60 °C into two sets of different intensities, which were assigned to cis and trans isomers on the basis of Faller's work.[8] The cis/trans ratio of 82:18 and $\Delta G^\ddagger = 12.3 \pm 0.5$ kcal/mol[9] are comparable to the values obtained for $C_5H_5Mo(CO)_2[PC_6H_5(OCH_3)_2]H$.[8] Heating of **2** in benzene gives neither further CO substitution nor bond opening of the phosphorane ligand by insertion of the metal hydride.[10]

Complex **2** reacts in $CHCl_3$ solution slowly with displacement of the metal hydride by chlorine to give complex **3**. The latter can be obtained more easily by direct reaction of phosphorane **1** with $C_5H_5Mo(CO)_3Cl$ in ether. The products of both reactions are identical in their physical properties and their infrared and ^1H and ^{31}P NMR spectra. They consist at room temperature of a mixture of two isomers, the cis configuration being preferred as in the analogous PR_3 (R = OCH_3, C_6H_5)[8] derivatives. The trans isomer is characterized by a doublet for the cyclopentadiene protons at 5.14 ppm with a coupling constant ^{31}P–H of 2.5 Hz and a ^{31}P resonance signal at 202 ppm. The cis/trans ratio was estimated by means of the C_5H_5 proton resonances as 94:6 ($CDCl_3$, 25 °C). Separation of the isomers by column chromatography[11] could not be realized because of their too strong absorption on SiO_2 and Al_2O_3. The high ν(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_5H_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 $[(C_5H_5)(CO)_2Mo(\text{phoran})]^+Cl^-$.

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_4PF_6 provokes the cationic chelate complex **5** to precipitate. Its analytical and spectroscopic data are in agreement with the proposed structure. The ν(NH) and ν(CO) infrared frequencies are increased by the positive charge on the metal atom. The ^{31}P 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 ^{13}C 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 η^5-$C_5H_5Mo(CO)_3X$ derivatives.[12]

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

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(8) (a) J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, **92**, 5852 (1970); (b) J. W. Faller, A. S. Anderson, and A. Jakubowski, *J. Organomet. Chem.*, **27**, C47 (1971).

(9) $k = 20.7$ s^{-1}, calculated by the slow-exchange method: A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *Phys. Inorg. Chem.*, **88**, 3185 (1966), and references cited therein.

(10) W. Beck, W. Danzer, and R. Höfer, *Angew. Chem., Int. Ed. Engl.*, **12**, 77 (1973).

(11) D. L. Beach, M. Dattilo, and K. W. Barnett, *J. Organomet. Chem.*, **140**, 47, (1977).

(12) L. J. Todd, J. R. Wilkinson, J. P. Hickey, D. L. Beach, and K. W. Barnett, *J. Organomet. Chem.*, **154**, 151 (1978), and references cited therein.

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 ν(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 reactions of $C_5H_5Mo(CO)_3Cl$, even in the presence of pyridine.

In summary, the reaction of (η^5-C_5H_5)$Mo(CO)_3H$ in THF with the bicyclophosphorane **1** (abbreviated phoran) gives $C_5H_5Mo(CO)_2$(phoran)H, **2**, which slowly converts in $CHCl_3$ solution to $C_5H_5Mo(CO)_2$(phoran)Cl, **3**. The same product can also be obtained from η^5-$C_5H_5Mo(CO)_3Cl$ and **1** in diethyl ether. Although a cationic form [$C_5H_5Mo(CO)_2$(phoran)]Cl of **3** may exist in traces, **3** can be converted in good yields into the [$C_5H_5Mo(CO)_2$(phoran)]PF_6 salt (**5**) by addition of NH_4PF_6 in aqueous ethanol. Reflux of **3** in benzene results in a further substitution of CO to give C_5H_5Mo(CO)(phoran)Cl, **4**. The ligand is monodentate and phosphorus-bound in **2** and **3** and bidentate in **4** and **5**, as shown in the ^{1}H, ^{13}C, and ^{31}P NMR.

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Chemical and X-ray Structural Properties of Bis[bis(diphenylphosphino)methane]carbonylrhodium(I) 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] hydrogenation using a rhodium chloride–diphosphine system,[4] and decarbonylation of aldehydes using a cationic bis(diphosphine)rhodium system.[5,6] In these cases where diphosphines of the type $Ph_2P(CH_2)_nPPh_2$ 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 $Rh[Ph_2(CH_2)_nPPh_2]_2^+$ 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 $Rh[Ph_2P(CH_2)_nPPh_2]_2CO^+$ is important and in some cases may be the rate-determining step.[7] Therefore, we set out to characterize these carbonyl complexes for n = 1 (dppm), 3 (dppp), and 4 (dppb). The n = 2 (dppe) analogue cannot be prepared[8] 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 $Rh(dppb)_2^+$ leads to dimeric products $Rh_2(dppb)_3(CO)_x$ with x = 2, 3, and 4. The characterization and structural properties of the dppb complexes will be published elsewhere.[9] The chemical and ^{31}P NMR properties of $Rh(dppm)_2CO^+$ and $Rh(dppp)_2CO^+$ and the single-crystal X-ray structure of the former are presented here. The solid-state structure of $[Rh(dppm)_2CO]BF_4$ is only the second crystallographic example of dppm chelating to a single Rh atom.[10]

Experimental Section

$^{31}P\{^1H\}$ 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% H_3PO_4 with positive shifts in parts per million upfield. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer. Hydrated rhodium(III) chloride was obtained on loan from Matthey Bishop, Inc., and bis(diphenylphosphino)methane (dppm) and 1,3-bis(diphenylphosphino)propane (dppp) were purchased from Strem Chemicals.

Synthesis of Compounds. $[Rh(dppm)_2]BF_4$. $Rh_2Cl_2(COD)_2$ (COD = 1,5-cyclooctadiene)[11] (140 mg, 0.57 mmol) was stirred in 25 mL of acetone under a purified N_2 atmosphere. Upon addition of $AgBF_4$ (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 dppm (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 N_2 atmosphere by using standard Schlenk techniques. The compound is air sensitive and may be recrystallized from dichloromethane–diethyl ether. Anal. Calcd for $RhC_{50}H_{44}P_4BF_4$: C, 62.65; H, 4.59. Found: C, 62.95; H, 4.55. $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6): δ 23.2, (d, J_{Rh-P} = 116 Hz).

$[Rh(dppm)_2CO]BF_4$. Gaseous CO was bubbled through a dichloromethane solution of $[Rh(dppm)_2]BF_4$ 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): ν(CO) 1945 cm^{-1}. Anal. Calcd for $RhC_{51}H_{44}OP_4BF_4$: C, 62.09; H, 4.46. Found: C, 61.79; H, 4.67. $^{31}P\{^1H\}$ NMR (25 °C, acetone-d_6): δ 22.5 (d, J_{Rh-P} = 98 Hz).

$[Rh(dppp)_2CO]BF_4$ was prepared in a manner analogous to that for the dppm complex from $[Rh(dppp)_2]BF_4$.[5] IR (KBr disk): ν(CO) 1929 cm^{-1}. Anal. Calcd for $RhC_{55}H_{52}OP_4BF_4$: C, 63.35; H, 4.99. Found: C, 62.98; H, 5.44. $^{31}P\{^1H\}$ NMR (−80 °C, acetone-d_6): δ −14.27 and 13.28 (A_2B_2X pattern, J_{Rh-P} = 86 and 113 Hz, J_{P-P} = 45 Hz, in good agreement with the literature values).[8]

X-ray Structure Determination. A crystal of $[Rh(dppm)_2CO]BF_4$ was fastened to the end of a thin glass fiber with 5-min epoxy resin. The dimensions of this ca. rectangular crystal were 0.25 × 0.20 × 0.20 mm. The crystal class 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 successfully solve and refine the structure (vide infra). The unit cell dimensions were determined by least-squares refinement of the angular values of 25 Mo Kα (λ = 0.71069 Å) peaks centered on a CAD 4 diffractometer[12] and are a = 11.281 (2) Å, b

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(2) Lando Summer Research Fellow, 1979.

(3) Kawabata, Y.; Hayashi, T.; Ogata, I. *J. Chem. Soc., Chem. Commun.* **1979**, 462.

(4) Poulin, J.-C.; Dang, T.-P.; Kagan, H. B. *J. Organomet. Chem.* **1975**, *84*, 87.

(5) Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 7083.

(6) Doughty, D. H.; McGuiggan, M. F.; Wang, H.; Pignolet, L. H. In "Fundamental Research in Homogeneous Catalysis"; Plenum: New York, 1979; Vol. 3, p 909.

(7) Doughty, D. H. Ph.D. Thesis, University of Minnesota, 1979.

(8) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120.

(9) Doughty, D. H.; Nowicki, S. C.; Pignolet, L. H., to be submitted for publication.

(10) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 1209.

(11) Chatt, J.; Venanzi, L. M. *J. Chem. Soc. A* **1957**, 4735.

(12) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described in the following references: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71; "CAD 4 SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978.

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