nating atom, and the, in some cases, relatively small spectral differences reflect chemically important variations in excited-state properties.

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Molybdenum(0) and Tungsten(0) Adducts of Some Bicyclic Aminophosphanes Having a P–N Bond in a Constrained Structure

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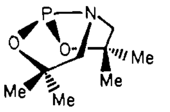
The coordination abilities of the bicyclic aminophosphanes **1a** and **1b**, which have P–N bonds in a strained structure that maintains both phosphorus and nitrogen atoms in a pyramidal configuration, have been evaluated with Mo(0) and W(0) carbonyls. A series of stable $M(CO)_{6-n}L_n$ adducts has been synthesized with M = Mo or W, $n = 1-3$, L = **1a** or **1b**, from $M(CO)_5$(pyridine), $M(CO)_4$(norbornadiene), and $M(CO)_3$(mesitylene). The ligands are coordinated through phosphorus only, as evidenced by the $\delta(^{31}P)$ displacements, the $J_{^{31}P-^{95,97}Mo} = 210$ Hz or $J_{^{31}P-^{183}W} \simeq 370$ Hz couplings, and the $\nu(CO)$ vibration patterns. Low steric requirements (the *cis*-$M(CO)_4(bcap)_2$ and *fac*-$M(CO)_3(bcap)_3$ isomers are formed readily and exclusively) and good π-accepting capabilities (on the basis of the high $\nu(CO)$ absorption frequencies) are the outstanding characteristics of these constrained ligands. No evidence for coordination through the nitrogen atom was found.

Introduction

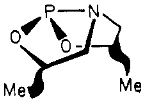
The coordinating ability of aminophosphanes in which nitrogen is directly bound to phosphorus is generally characterized by an increased donor character of the phosphorus atom at the expense of that of nitrogen. This and the planar configuration of the nitrogen atom, as well as the relatively shorter P–N bond lengths generally found, are usually interpreted as resulting from a $Np_\pi-Pd_\pi$ contribution to this bonding.[1]

Little work has been devoted to *constrained aminophosphanes*, i.e., aminophosphanes in which the nitrogen atom is prevented from being coplanar with its substituents. This being unfavorable to the overlap of the π orbitals, it should decrease the σ-donor ability of phosphorus, increase its π-accepting character, and make the nitrogen recover part of its own donor character. The very few, usually unstable, examples of N-bound BH_3 or BF_3 aminophosphane adducts known belong to this category.[2]

In the bicyclic aminophosphanes **1**,[3] abbreviated bcap, whose coordinating properties are evaluated here, the nitrogen atom is forced to a pyramidal configuration as a consequence of the pyramidal configuration of the phosphorus atom transmitted by the constraining bicyclic system. This decrease the $p_\pi-d_\pi$ interaction and hinders the draining of electron density from nitrogen toward phosphorus. The nitrogen atom of ligands **1** have indeed been shown to display a definite donor character by forming unusually stable adducts with BH_3 and BF_3.[2]



1a



1b

Where the ligand ability of phosphorus is concerned, this lowering of its σ-donor contribution due to the constrained structure could be partly compensated by the increased p character of the lone pair, by an increased π-acceptor character, and by a reduced cone angle at phosphorus, although the presence of one or two methyl groups on the carbon atoms α to the oxygen atoms may contribute to steric hindrance. The electron-withdrawing character of the oxygens is also expected to enhance the π-acceptor character of these ligands.

The aim of this study is to evaluate the coordinating properties of ligands **1** toward some low-valent transition-metal derivatives in order to situate their π-accepting character with respect to related ligands.[4-7] The choice of the rather soft molybdenum(0) and tungsten(0) carbonyls was further dictated by the surprising fact that the sole known example of coordination of a metal by a tricoordinated nitrogen atom bound to phosphorus has been observed in a tungsten carbonyl derivative of a phosphonitrilic compound.[8] In all the other cases reported so far, ligands having a P–N bond have been found to coordinate through phosphorus only.[9]

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Table I. ^{31}P NMR Data for $Mo(CO)_{6-n}(bcap)_n$ Adducts

adduct	ligand	δ-(^{31}P)[a]	Δ-(^{31}P)[b]	ref, solvent
$Mo(CO)_5L$	**1a**	188.8	26.3	*c*, toluene
	1b (α)	180.4	37.9	*c*, toluene
	1b (β)	187.0	37.4	*c*, hexane
	$P(OPh)_3$	154.3	26.5	12a
	$P(OCH_2)_3CC_2H_5$	137.3	45.5	12a
	$P(OCH_2CH_2)_3N$	143.7	28.5	12b
	$P(NMe_2)_3$	145.6	23.3	12c
$W(CO)_5L$	**1a**	162.5	0	*c*, toluene
	$P(OPh)_3$	131.3	3.5	12d
	$P(OCH_2)_3CC_5H_{11}$	115.0	22.2	9d
	$P(OCH_2CH_2)_3N$	119.2	4.0	12b
	$P(NCH_2)_3CC_5H_{11}$	112.0	25.4	9d
$Mo(CO)_4(L_2)$	**1a**, cis	192.8	30.3	*c*, CH_2Cl_2
	1b (α), cis	184.5	42.0	*c*, CH_2Cl_2
	$P(OMe)_3$ cis	152.4	30.1	12c
	$P(OMe)_3$ trans	159.4	37.1	12c
	$P(NMe_2)_3$ cis	164.0	23.0	12c
	$P(NMe_2)_3$ trans	174.0	33.0	12c
$W(CO)_4(L_2)$	**1b** (α), cis	160.0	17.5	*c*, CH_2Cl_2
	$P(OPh)_3$ cis	126.5	−1.3	12d
	$P(OPh)_3$ trans	133.5	5.5	12d
$Mo(CO)_3(L_3)$	**1a**, *fac*	193.2	30.7	*c*, CH_2Cl_2
	1b (α), *fac*	186.8	44.3	*c*, CH_2Cl_2
	$P(OMe)_3$ *fac*	166.0	25.0	12e
	$P(OMe)_3$ *mer*	165.0 (1 P)	24.0	12f
		177.0 (2 P)	36.0	
	$P(OEt)_3$, *mer*	164.0 (1 P)	26.0	12g
		172.0 (2 P)	34.0	
	PEt_3 *fac*	8.0	27.0	12c
	PEt_3 *mer*	15.7 (1 P)	34.7	12c
		25.5 (2 P)	44.5	

[a] δ taken positively downfield from H_3PO_4 85% as external reference. [b] $\Delta(^{31}P) = \delta(^{31}P)(adduct) - \delta(^{31}P)(free\ ligand)$. [c] This work.

Experimental Section

All manipulations were carried out under dry, deoxygenated argon, in Schlenk tubes or on a vacuum line. Solvents were purified according to conventional procedures and stored under argon. The ligands were synthesized as described in the literature.[3] The ^{31}P NMR spectra (Table I) were recorded with a WH 90 Bruker spectrometer operating in the Fourier transform mode.

Chemical shifts are given as positive when they occur at low fields with respect to 85% H_3PO_4 for ^{31}P. The infrared spectra (Tables II and III) were recorded with a Perkin-Elmer 577 spectrometer, and the mass spectra at 70 eV were recorded with a VG micromass 70-70F or R10 RIBERLAG L10. The elemental analyses were performed by the Service Central de Microanalyses of the CNRS.

[3,7-Dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane]-pentacarbonylmolybdenum(0) (2b). The ligand (91.0 mg, 0.57 mmol) was added to a solution of $Mo(CO)_5(py)$ (178 mg, 0.57 mmol) in 50 mL of hexane. The solution was stirred for 1 day at room temperature. Infrared monitoring showed the reaction then to be complete. Evaporation of the solvent yielded 200 mg of a white powder that was recrystallized three times from hexane at −80 °C and once from hexane/CH_2Cl_2 (10:2) at −30 °C, yielding 144 mg (64%) of small white crystals (mp 115–116 °C), readily soluble in most usual solvents. Anal. Calcd for $C_{11}H_{12}MoNO_7P$: C, 33.25; H, 3.02, Mo, 24.18; N, 3.53; P, 7.81. Found: C, 33.54; H, 3.01 Mo, 23.12; N, 3.55; P, 7.86. Mass spectrometry (M_r = 397.15; chemical ionization [ion], *m/e* for isotope ^{98}Mo (relative intensity)); MH_2^+, 401 (66.6%); MH^+, 400 (83.6%); M^+, 399 (99.6%); $[M - CO]^+$, 371 (34.1%); $[LH]^+$, 162 (100%).

[3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane]pentacarbonylmolybdenum(0) (2a). A similar procedure with 123 mg (0.65 mmol) of the ligand and 205 mg (0.65 mmol) of $Mo(CO)_5(py)$ in 50 mL of hexane gave, after stirring 3 days at room temperature, 230 mg of creamy white powder and, after the four recrystallizations, 150 mg (54%) of white needles (mp 107 °C), soluble in the usual solvents. Anal. Calcd for $C_{13}H_{16}MoNO_7P$: C, 36.71; H, 3.76; Mo, 22.59; N, 3.29; P, 7.29. Found: C, 36.69; H, 3.90; Mo, 22.40; N, 3.33; P, 7.45. Mass spectrometry (M_r = 425.21; chemical ionization [ion], *m/e* for isotope ^{98}Mo (relative intensity)): MH_2^+, 429 (41%); MH^+, 428 (79.4%); M^+, 427 (100%); $[M - H]^+$, 426 (91.1%); $[M - CO]^+$, 399 (8.8%).

[3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane]pentacarbonyltungsten(0) (3a). A similar procedure applied to 134 mg (0.71 mmol) of the ligand and 282 mg (0.70 mmol) of $W(CO)_5(py)$ in 100 mL of hexane yielded, after 10 days of stirring at room temperature (IR monitoring showed the reaction then to be complete) and evaporation of the solvent, 360 mg of a yellow powder,

Table II. ν(CO) (cm^{-1}) Vibration Frequencies in $M(CO)_5L$ (M = Mo, W) Adducts

	Mo				W				
ligand	$A_1^{(2)}$ (m)	B_1 (w)	$A_1^{(1)}$ (s)	E (s)	$A_1^{(2)}$ (m)	B_1 (w)	$A_1^{(1)}$ (s)	E (s)	solvent or ref
1a	2098	2006	1976	1966	2088	1988	1958	1948	hexane
1b	2095	1978	1972	1962					hexane
PCl_3	2095	2013	2001	1988					4
$P(OPh)_3$	2085	2000	1972	1967	2083		1965	1957.5	4–9d
$P(OCH_2)_3CC_5H_{11}$					2085.5	1989	1963.5	1958	9d
$P(OCH_2)_3CC_3H_7$	2084	1987	1963	1963					14a
$P(OCH_2CH_2)_3N$	2078		1956	1956	2078		1956	1948	13
$P(OEt)_3$	2080	1995	1966	1952	2078		1959	1944	4–9d
$P[N(CH_3)CH_2]_3CC_5H_{11}$					2071		1949	1943	9d
$P(NMe_2)_3$	2073	1986	1949	1942	2070	1971	1940	1940	14b–9d
$P(SCH_2)_3CC_5H_{11}$					2081	1990	1965	1959	9d
$P(CH_2O)_3CC_4H_9$					2079	1983	1965	1951	9d
$P(CH_2N)_3(CH_2)_3$	2070		1958	1948	2070		1954	1943	14c
$P(Ph)_2CH_2CH_2NEt_2$	2078		1954	1948	2076		1950	1939	9b
$P(Me)_2CH_2CH_2P(Me)_2$	2073	1984	1955	1944	2071	1975	1949	1949	14d
$P(CH_2CH_2CN)_3$	2077		1965	1952					7
PPh_3	2073		1945	1949	2072		1947	1942	7–9d
C_5H_5N	2076		1922	1943	2080		1920	1933	10

Table III. ν(CO) (cm^{-1}) Absorption Frequencies in *cis*- and *trans*-$M(CO)_4(L_2)$ (M = Mo, W) Adducts

	cis-$Mo(CO)_4(L_2)$				*trans*-$Mo(CO)_4(L_2)$			*cis*-$W(CO)_4(L_2)$				
ligand	$A_1^{(2)}$ (m)	$A_1^{(1)}$ (s)	B_1 (vs)	B_2 (s)	A_1 (gw)	B_1 (gw)	E_u (vs)	$A_1^{(2)}$ (m)	$A_1^{(1)}$ (s)	B_1 (vs)	B_2 (s)	solvent or ref
1a	2042	1936	1919	1900								CH_2Cl_2
1b (α)	2040	1945	1920	1900				2042	1985	1950	1930	CH_2Cl_2
$P(OCH_2)_3CC_3H_7$	2046	1959	1939				1939	2046		1956	1933	14a
$P(OMe)_3$	2037	1946	1926	1921	2035	1969	1921	2034	1947	1939	1914	12a, 17a
$P(Ph)_2C_2H_4NEt_2$	2019	1905	1893	1849				2013	1898	1884	1884	17b
$NMe_2C_2H_4NMe_2$	2013	1890	1875	1837								17c

and after the four recrystallizations, 200 mg (56%) of white needles (mp 118 °C), soluble in the usual solvents. Anal. Calcd for $C_{13}H_{16}NO_7PW$: C, 30.41; H, 3.12; N, 2.73; P, 6.04; W, 35.87. Found: C, 30.48; H, 3.07; N, 2.76; P, 6.51; W, 37.57. Mass spectrometry (M_r = 513.12; [ion], *m/e* for isotope ^{184}W (relative intensity)): MH^+, 514 (5.0%); M^+, 513 (35.1%); $[M - 2CO]^+$, 457 (9.5%); $[M - 3CO]^+$, 429 (37.0%); $[M - 5CO]^+$, 373 (100%).

Bis[3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)-octane]tetracarbonylmolybdenum(0) (4a). The ligand (620 mg, 3.28 mmol) was added to a solution of $Mo(CO)_4(nbd)$ (490 mg, 1.63 mmol) in 80 mL of CH_2Cl_2. The reaction was complete after 18 h of stirring at room temperature. Evaporation of the solvent gave 850 mg of a light beige powder. This was washed twice with 2 mL of pentane and recrystallized from hexane/CH_2Cl_2 (7:3) at -30 °C to yield 750 mg (79%) of large square, light yellow crystals, mp 181 °C dec, soluble in CH_2Cl_2 and CH_3CN, sparingly soluble in hydrocarbons. Anal. Calcd for $C_{20}H_{32}MoN_2O_8P_2$: C, 40.96; H, 5.46; Mo, 16.38; N, 4.79; P, 10.58. Found: C, 40.74; H, 5.22; Mo, 16.36; N, 4.78; P, 10.53. Mass spectrometry (M_r = 586.43; chemical ionization [ion], *m/e* (relative intensity)): MH_2^+, 590 (62.9%); MH^+, 589 (84.4%); M^+, 588 (100%); $[LH]^+$, 190 (68.1%).

Bis[3,7-dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane]-tetracarbonylmolybdenum(0) (4b). A solution of 805 mg (5 mmol) of **1b** in 10 mL of CH_2Cl_2 was added to a solution of 750 mg (2.5 mmol) of $Mo(CO)_4(nbd)$ dissolved in 20 mL of CH_2Cl_2. After 17 h of stirring at room temperature, the solution was concentrated and 10 mL of hexane was added. The brown powder that precipitated was filtered, washed three times with 2 mL of hexane, dried, and recrystallized from CH_2Cl_2/hexane to yield 690 mg (50%) of a light brown compound (mp 110 °C dec) soluble in CH_2Cl_2 and CH_3CN and insoluble in aliphatic and aromatic hydrocarbons. Anal. Calcd for $C_{16}H_{24}MoN_2O_8P_2$: C, 36.22; H, 4.56; Mo, 18.09; N, 5.28; P, 11.68. Found: C, 36.04; H, 4.64; Mo, 18.02; N, 5.26; P, 11.75. Mass spectrometry (M_r = 530.30; [ion], *m/e* for isotope ^{98}Mo (relative intensity)): M^+, 532 (6%); $[M - CO]^+$, 504 (5%); $[M - 3CO]^+$, 448 (24%); $[M - 4CO]^+$, 420 (18%); $[L]^+$, 161 (11%); $[C_4H_8NOP]^+$, 117 (100%).

Bis[3,7-dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane]-tetracarbonyltungsten(0) (5b). A solution of 512 mg (3.18 mmol) of **1b** in 30 mL of CH_2Cl_2 was added to 414 mg (1.06 mmol) of $W(CO)_4(nbd)$. After 36 h of stirring at room temperature, the solution was concentrated, and 15 mL of pentane was added. The adduct that precipitated was filtered, washed three times with 5 mL of pentane, and dried under vacuum to yield 461 mg (70%) of transparent crystals (mp 126–128 °C dec) sparingly soluble in CH_2Cl_2. Anal. Calcd for $C_{16}H_{24}N_2O_8P_2W$: C, 31.09; H, 3.91; N, 4.53; P, 10.02; W, 29.74. Found: C, 31.12; H, 3.86; N, 4.53; P, 10.07; W, 28.04%. Mass spectrometry (M_r = 618.21; [ion], *m/e* for isotope ^{184}W (relative intensity)): M^+, 618 (22%); $[M - 2CO]^+$, 562 (43%); $[M - 3CO]^+$, 534 (16%); $[M - 4CO]^+$, 506 (86%); $[C_4H_8NOP]^+$, 117 (64%).

Tris[3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo-(3.3.0)octane]tricarbonylmolybdenum(0) (6a). $Mo(CO)_3(mes)$ (346 mg, 1.15 mmol) was added to a solution of the ligand (670 mg, 3.54 mmol) in CH_2Cl_2 (80 mL). The reaction was complete after 24 h of stirring at room temperature. The white-beige powder (784 mg) obtained after evaporation of the solvent was washed three times with 3 mL of pentane and recrystallized from hexane/CH_2Cl_2 (10:2) at -30 °C to yield 620 mg (72%) of white parallelepipedic crystals, mp 190 °C dec, soluble in CH_2Cl_2 and CH_3CN and sparingly soluble in hydrocarbon solvents. Anal. Calcd for $C_{27}H_{48}MoN_3O_9P_3$: C, 43.37; H, 6.43; Mo, 12.85; N, 5.62; P, 12.45. Found: C, 43.11; H, 6.51; Mo, 12.73; N, 5.62; P, 12.47. Mass spectrometry (M_r = 747.64; chemical ionization [ion], *m/e* for isotope ^{98}Mo (relative intensity)): MH_5^+, 754 (61%); MH^+, 750 (96.3%); M^+, 749 (100%); $[M - CO]^+$, 721 (45.3%); $[M - 2CO]^+$, 693 (33.8%); $[M - 3CO]^+$, 665 (46.6%); $[LH]^+$, 190 (100%).

Tris[3,7-dimethyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octane]tricarbonylmolybdenum(0) (6b). $Mo(CO)_3(mes)$ (360 mg, 1.20 mmol) was added to a solution of 600 mg (3.74 mmol) of the ligand in 30 mL of CH_2Cl_2. After 1 h at room temperature, the solution changed from yellow to deep orange. The precipitate that formed by addition of 10 mL of pentane to the concentrated solution was filtered, washed three times with 2 mL of pentane, and dried to yield 360 mg (54%) of a brown solid (mp 160 °C) soluble in CH_2Cl_2 and CH_3CN. Anal. Calcd for $C_{21}H_{36}MoN_3O_9P_3$: C, 38.02; H, 5.47; N, 6.33. Found: C, 36.98; H, 5.34; N, 5.86%. Mass spectrometry (M_r = 663.46; [ion], *m/e* for isotope ^{98}Mo (relative intensity)): M^+, 665 (1%); $[M - 3CO - L]^+$, 420 (3%); $[MoC_4H_8NOP]^+$, 215 (100%); $[L]^+$, 161 (7%); $[C_4H_8NOP]$, 117 (59%).

Results and Discussion

Our initial attempts to obtain molybdenum carbonyl adducts of bicycloaminophosphanes by direct substitution of $M(CO)_6$ (M = Mo, W) failed: after 48 h at 120 °C, only small amounts of CO had evolved from an equimolar mixture of $Mo(CO)_6$ and **1b**, and this approach is all the more unsuitable because of the tendency of the ligand to polymerize.[3] The photochemical activation was as unsuccessful as the thermal activation procedure: after 48 h of irradiation (Hanovia lamp of 125 W) of a 1:1 mixture of $W(CO)_6$ and **1b**, the infrared spectra showed only little complexation while ^{31}P NMR showed intensive degradation of the ligand.

By contrast, well-defined mono-, di-, and trisubstituted $M(CO)_{6-n}(bcap)_n$ adducts could be obtained at room temperature when some of the carbonyl groups were first substituted by the more labile pyridine (py), norbornadiene (nbd), or mesitylene (mes) ligands.

Molybdenum(0) and Tungsten(0) Pentacarbonyl Bicycloaminophosphane Adducts 2 and 3. The monosubstituted metal carbonyl adducts $M(CO)_5(bcap)$ **2** (M = Mo) and **3** (M = W) were prepared from $M(CO)_5(py)$[10] by allowing it to react with equimolar quantities of **1a** or **1b**. The displacement of pyridine occurred at room temperature. Infrared monitoring showed that the reaction is about 3 times slower with W than with Mo and also about 3 times slower with the sterically more hindered **1a** as compared to **1b**. The crude reaction products were contaminated by ca. 10% of impurities, which needed repeated recrystallizations to be eliminated, thus lowering the final yields (54–64%). The coordination of the metal by the two diastereoisomers (α and β) of **1b**[3] occurred equally well, and contrary to what had been observed in the presence of B_2H_6,[2] no epimerization of the ligand was found. The initial 4:1 ratio of the two isomeric free ligands was conserved upon coordination, as shown by ^{31}P NMR analysis of the crude reaction mixture, but only the adduct of the most abundant, 2,2′-endo,endo isomer[3b] was isolated.

The isolated compounds are thermally stable and soluble in most common solvents but highly air sensitive. Their composition was checked by elemental analysis and their molecular complexity by mass spectrometry using chemical ionization to insure that adducts of the easily formed dimers of the ligands had not been obtained.[3]

The coordination of the ligands through phosphorus is evidenced by the NMR spectra, which exhibit the expected displacements (larger with Mo than with W)[11] of the ^{31}P resonance toward lower fields, as well as by the characteristic phosphorus–metal ^1J coupling in the case of tungsten. The $\delta(^{31}P)$ data are collected in Table I, together with some found in the literature for related $M(CO)_5L$ adducts.

The relatively high value (366 Hz) of the $^1J_{^{31}P-^{183}W}$ coupling is closer to those found in $W(CO)_5L$ with symmetrical phosphites such as $P(OEt)_3$ (391 Hz) of $P(OCH_2)_3CC_5H_{11}$ (393 Hz) than for amides: $P(NMe_2)_3$ (297 Hz) or $P[N(CH_3)CH_2]_3CC_5H_{11}$ (318 Hz).[9d,13]

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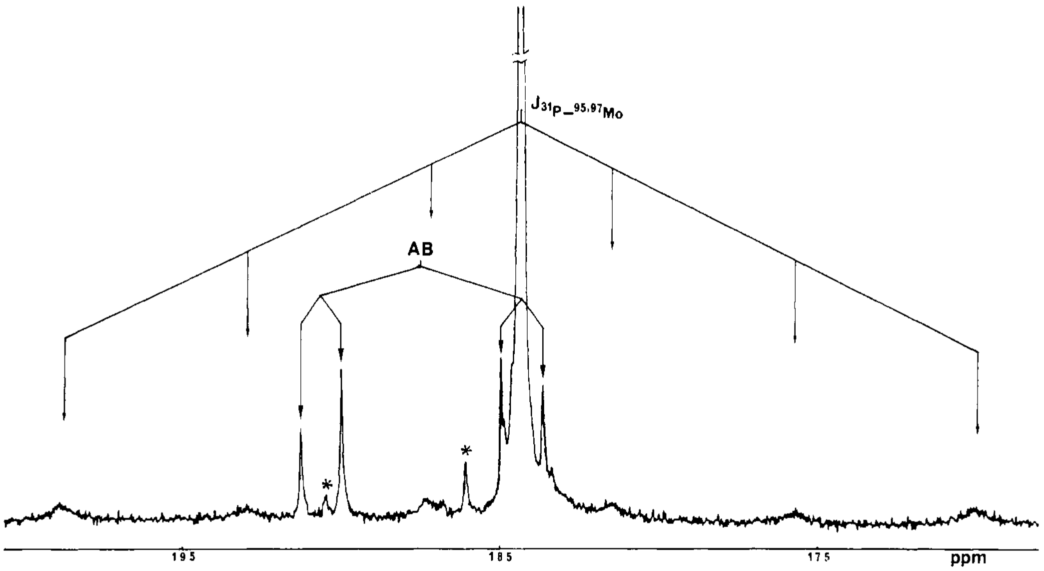

Figure 1. Proton-decoupled ^{31}P NMR spectra of $(CO)_4Mo[P(OCH(CH_3)CH_2)_2N]_2$ (**4b**), 0.2 M in CH_2Cl_2. The asterisks refer to signals that were not assigned.

The ν(CO) vibration frequencies are collected in Table II, where they are compared to those of related $Mo(CO)_5L$ adducts having other phosphorus- or nitrogen-based ligands. All the *mono*aminophosphane adducts reported here exhibit four ν(CO) vibrations, which are assigned to the 2 A_1 + E modes expected for C_{4v} symmetry and to the B_1 mode, which becomes active when the ligand lowers the local symmetry at the metal. The relatively high frequencies observed further confirm that coordination occurs through the phosphorus atom rather than through the nitrogen atom[4,15] and reflect its good π-accepting character. Furthermore, the $A_1^{(1)}$ vibration is found at higher frequency than the E mode vibration, while the contrary would have been expected if the ligands were N-coordinated.[4,15]

It is noteworthy that the A_1 and E frequencies found for adducts of **2** are the highest in Table II, but for those of PCl_3. They are higher than those found with $P(OPh)_3$ or with the larger, less strained bicyclic ligands $P(OCH_2)_3CR$ and are rated among those which display the highest acceptor/donor ratio.[6]

Molybdenum and Tungsten Tetracarbonyl Bis(bicycloaminophosphane) Adducts 4 and 5. Molybdenum tetracarbonyl norbornadiene[16] reacted at room temperature with 2 molar equiv of **1a** and **1b** to give the air-sensitive but thermally stable compounds **4** (M = Mo) and **5** (M = W). The increased lability of norbornadiene with respect to pyridine results in shorter reaction times. The 2:1 ligand:metal ratio was established by elemental analysis and mass spectrometry. When a twofold excess of $M(CO)_4$(nbd) was used, the same adducts were obtained, while the excess of starting material was recovered unreacted.

Compound **4a** presents a single signal in the ^{31}P NMR of the crude reaction mixture and therefore consists of a single isomer. The coordination by phosphorus is attested to by the displacement of the ^{31}P resonance toward lower fields with respect to the free ligand (Table I). The $\delta(^{31}P)$ of cis adducts is close to that of the monosubstituted adduct in accordance with the fact that the phosphorus atoms are in both cases trans to CO groups.[12c]

This assignment is also supported by four ν(CO) vibrations (2 A_1 + B_1 + B_2) in the infrared spectra, while only the E_u mode should be active in the trans isomer (although the A_{1g} and B_{1g} modes can become active when the ligand lowers the symmetry at the metal). Table III compares the ν(CO) frequencies of the bicycloaminophosphane adducts with those of related *cis*- or *trans*-$Mo(CO)_4L_2$ adducts, where L_2 can also represent bidentate symmetric or mixed phosphorus–nitrogen ligands. Again, the ν(CO) frequencies would have been expected to be lower if coordination had occurred through nitrogen.

Since the free ligand **1b** consists of a 4:1 mixture of two diastereoisomers, one expects the formation of three isomeric $Mo(CO)_4(bcap)_2$ adducts in 16:4:1 relative ratios, provided there is no interconversion between the two diastereoisomeric ligands upon coordination[2] and provided their distribution on the metal is stochastic. Accordingly, one finds an intense singlet (80% of total peak area) in the proton-decoupled ^{31}P spectra of adduct **4b** (Figure 1). This singlet is accompanied by an AB system (18% of total peak area, δ_{P_α} 184.5; δ_{P_β} = 190.7 ppm; $J_{P_\alpha-P_\beta}$ = 41 Hz), as expected for the second most abundant isomeric adduct in which the metal would bear two distinct ligands in cis configuration. The difference in chemical shifts of δ 6.2 between the two phosphorus atoms is close to that which is found in the two distinct uncomplexed isomeric ligands (δ 7.2).[3] No attempt was made to identify the singlet expected from the third adduct, in view of its low proportion.

The broad (ca. 20–30 Hz line width at midheight) satellite sextuplets due to the $^1J_{^{31}P-^{95,97}Mo}$ couplings (^{95}Mo (15.7%) and ^{97}Mo (9.5%), both having $I = {}^5/_2$ and close magnetic moments) are well detected (Figure 1). Their values of 210 Hz are very close to that found by Verkade et al.[12a] for $Mo(CO)_5P(OEt)_3$ (214 Hz) in spite of the lower electronegativity of one of the phosphorus' substituents (cf. $Mo(CO)_5P(NMe_2)_3$, 173 Hz).

The $W(CO)_4(bcap)_2$ adduct of **1b** displays a very similar ^{31}P NMR spectrum, with a main singlet (ca. 90% of total peak area) at 160 ppm and an AB system centered at 165.6 ppm. The P–W coupling is evident in the satellites on the main peak ($^1J_{^{31}P-^{183}W}$ = 370 Hz).

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The cis configurations of the main isomers of **4b** and **5b**, isolated by recrystallization, are further attested to by the four ν(CO) stretching vibrations. They appear in the infrared spectra at values close to those found for the other cis adducts (Table III).

The fact that only the cis isomer has formed even with ligand **1a** shows that its four methyl groups on the carbon α to the oxygen atoms do not contribute sufficiently to steric hindrance to destabilize the cis configuration in favor of a trans configuration.

While ligands having unconnected P and N donor sites have been found to behave as bidentate donors with respect to group 6 metal carbonyls,[9a,b] no evidence for the formation of adducts in which ligands **1a** or **1b** act in a bidentate fashion, either in mononuclear or in bridged species, was obtained with $M(CO)_4(nbd)$ (M = Mo, W), even though two sites were made readily available in the coordination sphere of the metal.

Molybdenum Tricarbonyl Tris(bicycloaminophosphane) Adducts. Trisubstituted adducts of $M(CO)_3(bcap)_3$, with M = Mo, were obtained when $M(CO)_3(mes)$[18] was allowed to react with 3 molar equiv of the ligands. Both adducts are thermally stable. No evidence for the formation of compounds having other stoichiometries such as, for example, $M(CO)_3(bcap)_2$, where one of the ligands could exhibit a bidentate behavior, was found.

Only the *fac* isomer was observed to form in both CH_2Cl_2 and benzene as solvents,[19] as evidenced by a single signal in the proton-decoupled ^{31}P NMR spectra of the crude reaction mixture with ligand **1a**. The values of the chemical shifts are close to those found in the mono- and cis disubstituted adducts, as expected, since the phosphorus atoms are comparably located trans to CO groups (Table I). The P-Mo coupling satellites confirm that coordination occurs through phosphorus ($^1J_{^{31}P-^{95,97}Mo}$ = 210 Hz). The ν(CO) vibrations in CH_2Cl_2 further establish a *fac* configuration of the adduct since they consist of two absorptions, the A_1 and E modes, at 1966 (s) and 1879 (vs) cm^{-1}, expected for C_{3v} symmetry, while the *mer* configuration should give three active modes ($2\ A_1 + B_1$).[17a]

Similar conclusions were reached for the isolated adduct of ligand **1b**, which consists of the most abundant of the five possible isomers expected from the various possible combinations of the two diastereoisomeric ligands on the metal.

Characteristic Features of the Bicyclic Aminophosphanes 1 as a Ligand. Consistent behavior of the ligand and consistent spectral characteristics of the adducts were found throughout the series of the eight $M(CO)_{6-n}(bcap)_n$ compounds we prepared. They may be summarized as follows. Both constrained aminophosphanes readily give stable zerovalent Mo and W complexes. Coordination always occurs through phosphorus. Only the cis isomers and *fac* isomers are formed when n = 2 or 3, respectively. The ν(CO) frequencies rank among the highest found with phosphorus ligands in such adducts.

These data are all consistent with (1) a high π-accepting capability, better, on the basis of the ν(CO) infrared data, than those of $P(OCH_3)_3$, $P(OCH_2)_3CR$, or $P(CH_2CH_2CN)_3$, and (2) low steric hindrance, lower than those of these latter ligands, although the two contributions cannot be separated. Both arise from the constraints due to the bicyclic structure of the bcap ligands.

These features are further corroborated by the very short P-Fe bond length (2.105 Å) found in $(\eta^5\text{-Cp})Fe(Ph)(CO)[\overline{P(OCH_2CH_2)_2N}]$ compared to 2.23 Å for the related PPh_3 adducts.[20] This shortening (0.12 Å) is significantly greater than that found in $M(CO)_5L$ (M = Cr, Mo) adducts, on progressing from PPh_3 to $P(CH_2CH_2CN)_3$ (0.06 Å). The latter ligand has recently been described as a good π acceptor.[7]

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Registry No. **2a**, 79201-51-7; **2b** (α), 79201-52-8; **2b** (β), 79254-37-8; **3a**, 79201-53-9; **4a**, 79201-54-0; **4b** (α,α), 79215-51-3; **4b** (α,β), 79201-55-1; **5b** (α,α), 79201-56-2; **6a**, 79215-50-2; **6b** (α,α,α), 79215-52-4; $Mo(CO)_5(py)$, 14324-76-6; $W(CO)_5(py)$, 14586-49-3; $Mo(CO)_4(nbd)$, 12146-37-1; $W(CO)_4(nbd)$, 12129-25-8; $Mo(CO)_3(mes)$, 12089-15-5.

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Reaction of (Chlorophosphine)iron Tetracarbonyl Complexes with Aluminum Chloride. Iron Tetracarbonyl Complexes of Two-Coordinate Phosphorus Cations

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The (chlorophosphine)iron tetracarbonyl complexes $Me_2NP(Cl)_2Fe(CO)_4$, $(Et_2N)_2P(Cl)Fe(CO)_4$, $(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$, $[(Me_3Si)_2N]_2P(Cl)Fe(CO)_4$, and $(t\text{-}Bu)(Me_2N)P(Cl)Fe(CO)_4$ have been prepared by reaction of the corresponding phosphorus(III) chlorides with $Fe_2(CO)_9$ in hexane solution. These $Fe(CO)_4$ complexes have been characterized by elemental analysis and ^{31}P NMR, ^{13}C NMR, and IR spectroscopy. The coordinated phosphenium ions $[(Me_2N)P(Cl)Fe(CO)_4]^+$, $[(Et_2N)_2PFe(CO)_4]^+$, $[(i\text{-}Pr_2N)_2PFe(CO)_4]^+$, $[((Me_3Si)_2N)_2PFe(CO)_4]^+$, and $[(t\text{-}Bu)(Me_2N)PFe(CO)_4]^+$ have been prepared as their $AlCl_4^-$ salts by treatment of the respective precursor (chlorophosphine)iron tetracarbonyl complexes with the stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution. These phosphenium ion complexes have been identified by elemental analysis and ^{31}P NMR, ^{13}C NMR, and IR spectroscopy. The π-acceptor nature of phosphenium ion ligands is discussed on the basis of various spectroscopic data.

Introduction

Recent years have witnessed an increasing concern with the chemistry of coordinatively unsaturated cations which feature main-group elements other than carbon as the central atom. At present, the best known of these species are the two-coordinate phosphorus cations of general formula R_2P^+ (phosphenium ions).[2] Since the six-valence-electron phosphenium

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