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Reaction of Constrained Bicyclic Aminophosphanes with Cyclopentadienyltricarbonylmolybdenum(II) Derivatives. Investigations into the Basicity of the Nitrogen Site

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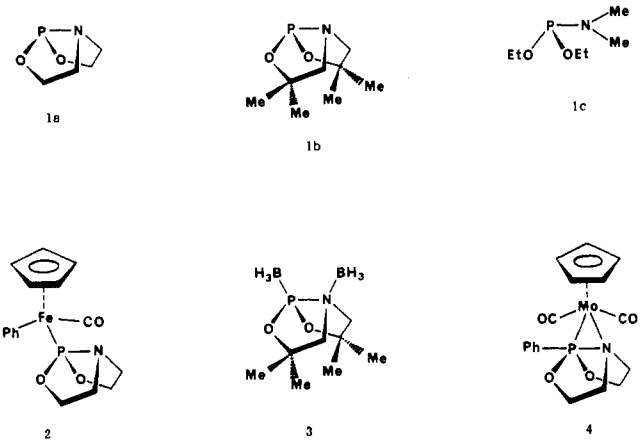
The donor ability of constrained bicyclic aminophosphane ligands $\overline{P(OCH_2CH_2)_2N}$ (**1a**) and $\overline{P(OCMe_2CH_2)_2N}$ (**1b**) has been evaluated and compared with that of their acyclic analogue $(EtO)_2PNMe_2$ (**1c**) toward a series of $CpMo(CO)_3X$ derivatives (X = H, Cl, CH_3). A CO group in $CpMo(CO)_3Cl$ is readily substituted at room temperature; further substitution requires photochemical activation. Coordination always occurs through P. The ν(CO) frequencies of the adducts indicate a higher π-accepting character for the bicyclic ligands than for the nonconstrained analogue. Gaseous HCl provokes the quaternization of the nitrogen site in $HCpMo(CO)_2$ (**1b**), which thus displays definite basicity while retaining the P–N bond; in contrast, HCl cleaves the P–N bond of the adduct of the noncyclic **1c**. The first stable compound with a protonated P-bound nitrogen could thus be isolated and was fully characterized.

Introduction

The $>P^{III}-N<$ assemblage, as found in aminophosphanes, has to be considered as an entity in itself. Its behavior, and in particular the donor character of the phosphorus and nitrogen sites, bears little resemblance to that of the two elements taken separately, as when found in phosphanes or in amines. Thus, in the absence of constraints, a P-bound tricoordinate nitrogen is seen to adopt a configuration in which it is coplanar with its substituents, while it essentially loses its basicity toward Lewis acids to the benefit of phosphorus.[1] This is usually attributed to the existence of a $N(p_\pi)-P(d_\pi)$ contribution to the bonding, which drains the lone-pair electrons of nitrogen into the d orbitals of phosphorus.

The bicyclic aminophosphanes of types **1a** and **1b**,[2] the object of this study, have a constrained structure, which transmits the pyramidal geometry of the phosphorus atom to the nitrogen atom.



The extent to which this nitrogen, while retaining its pyramidal configuration, also retains its donor ability was an appealing question. It is clear from symmetry considerations that the absence of planarity does *not* forbid $N(p_\pi)-P(d_\pi)$ interaction from taking place.[3] This point is borne out by the shortness of the P–N bond (1.68 Å) in compound **2**,[4] in spite of the marked pyramidal character of the nitrogen (sum of angles, $\sum N$, around N = 333°), when compared with that found in **3** (1.76 Å),[5] in which the nitrogen atom's lone electron pair is no longer available for donation. The unusually strong donor character of nitrogen in **1a** and **1b** has been established by the formation of *stable* nitrogen-bound BF_3 and BH_3 adducts.[5] In the presence of a variety of Mo(0) and W(0) derivatives, these ligands have so far always behaved as monodentates bound through the phosphorus atom only. They were shown to exhibit low steric requirements and a strong π-accepting character.[6] The lesser σ-donor character of phosphorus that would result from a weakening of the $N(p_\pi)-P(d_\pi)$ donation could indeed be compensated for by an increased π-acceptor character.

The purpose of the present study is to further establish the differences in behavior and coordinating ability of these constrained bicyclic ligands with respect to their open-chain analogues; $(EtO)_2PNMe_2$[7] (**1c**) was chosen for this comparison. The basicity of the nitrogen atom was a matter to which we paid particular attention. The choice of cyclopentadienyltricarbonylmolybdenum(II) derivatives as substrates was dictated by several considerations: (1) The oxidation of molybdenum being higher than that in previous work, it was expected to favor coordination at nitrogen.[8] (2) The first compound known in which *both* phosphorus and nitrogen atoms of a P–N bond (though the former is in a 5-coordinated P(III) state) are bound to a transition metal, **4**, was a $CpMo(CO)_2$ derivative.[9] (3) It was worthwhile to test whether the observation made in the case of the cyclopentadienyliron(II) derivative, **2**, that an aryl group could be transferred from the metal to the phosphorus site of the ligand, with concomitant opening of the P–N bond under the action of HCl,[4] could be extended to other, related compounds. Alternative possible results of this action of HCl on the phosphorus-bound adducts of **1** could cause the breaking of the P–N bond with formation of a P–Cl bond,[10,11] the transfer of a substituent from

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Table I. Proton and Phosphorus NMR Data for Compounds **5–10** (J in Hz)

	$^{31}P\{^1H\}$[a,b]			^1H[b]					
compd	$\delta(^{31}P)$	cis/trans ratio	solvent	$\delta(C_5H_5)$	$^3J_{H-P}$	δ(M–H)	$^2J_{H-P}$	cis/trans ratio	solvent
cis/trans-**5b**	219.9 (s)	70/30	toluene	4.96 (s)		−5.95 (d)	50.7	68/32	toluene-d_8
cis-**5b**[c]	216.8 (s)			4.87 (s)		−6.02 (d)	61.0		
trans-**5b**[c]	225.5 (s)			4.82 (s)		−5.73 (d)	27.1		
cis-**6a**	200.7 (s)	86/14	$CHCl_3$	5.52 (s)				85/15	$CDCl_3$
trans-**6a**	220.2 (s)			5.38 (d)	2.35				
cis-**6b**	201.4 (s)	82/18	$CHCl_3$	5.51 (s)				80/20	$CDCl_3$
trans-**6b**	217.7 (s)			5.40 (d)	2.25				
cis-**6c**	164.9 (s)	97/3	$CHCl_3$	5.48 (s)				96/4	$CDCl_3$
trans-**6c**	182.8 (s)			5.28 (d)	2.25				
trans-**7b**[d]	223.7 (s)		toluene	5.20 (d)	0.88				C_6D_6
trans-**8a**	212.8		toluene	5.34 (s)					toluene-d_8
trans-**8c**	174.8		toluene	5.19 (t)	1.0				toluene-d_8
(**9b**)(Cl^-)	215.0 (s)		THF	5.53 (s)		−6.73 d	61.7		CD_3CN
cis-**10c**	185.7 (s)	93/7	$CHCl_3$	5.53 (s)				92/8	$CDCl_3$
trans-**10c**	204.6 (s)			5.44 (d)	2.70				

[a] ^{31}P NMR data for the free L: **1a**, $\delta(P) = 139.9$; **1b**, $\delta(P) = 162.5$, $^3J_{H_AP} = 8.25$ Hz, $^3J_{H_BP} = 9$ Hz; **1c**, $\delta(P) = 144.4$. [b] s = singlet; d = doublet. [c] Determined at −40 °C. [d] $\delta(-COCH_3) = 2.99$.

Table II. ν(CO) Vibrations in $CpMo(CO)_2LX$ Adducts (X = H, Cl; L = **1a**, **1b**, **1c**)

	$CpMo(CO)_2LH$			$CpMo(CO)_2LCl$			$CpMo(CO)L_2Cl$	
L	ν_s (vs)[a]	ν_{as} (vs)	solvent	ν_s (vs)	ν_{as} (vs)	solvent	ν (vs)	solvent
1a				1994	1914	$CHCl_3$	1840	toluene
1b	1960	1895	cyclohexane	1980	1900	$CHCl_3$		
1c				1976	1889	$CHCl_3$	1799	toluene
[**1bH**]$^+$	1950	1879	THF					
$PCl(OEt)_2$				1992	1913	$CHCl_3$		

[a] vs = very strong.

the metal to phosphorus with concomitant opening of the P–N bond, or the hitherto unreported quaternization of the nitrogen site of the intact aminophosphanes, as was found here. Finally, we also tested whether the action of $[Fe(NO)I]_2$, which is known to give $Fe(NO)_2IL$ adducts with various amines (L),[12] would lead to a nitrogen-coordinated aminophosphane.

Experimental Section

All manipulations were carried out under dry, deoxygenated argon, in Schlenk tubes or on the vacuum line. Solvents were purified according to conventional procedures, and stored under argon. The ligands,[2] as well as the $CpMo(CO)_3X$ derivatives,[13] were synthesized as described in the literature. The ^1H and ^{31}P NMR spectra (Table I) were recorded with a Bruker Fourier transform WH 90 spectrometer. Chemical shifts are given positively toward low fields with respect to Me_4Si for ^1H NMR and with respect to 85% H_3PO_4 for ^{31}P NMR. The IR spectra (Table II) were recorded with a Perkin-Elmer 577 spectrometer, and the mass spectra were recorded at 70 eV with a Nermag R-1010 spectrometer. The elemental analyses were performed by the Service Central de Microanalyses of the CNRS.

(3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane)hydridodicarbonyl(η^5-cyclopentadienyl)molybdenum(II) (5b). Ligand **1b** (620 mg, 3.28 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ (800 mg, 3.25 mmol) in 20 mL of pentane. The yellow-white powder that precipitated immediately was washed with 3 × 5 mL of pentane, dried on the vacuum line for a night, and recrystallized from toluene/pentane (1/2) at −30 °C, to yield 925 mg (70%) of light-yellow crystals, mp 75 °C dec, soluble in benzene, toluene, acetonitrile, and dichloromethane. Anal. Calcd for $C_{15}H_{22}MoNO_4P$: C, 44.10; H, 5.40; Mo, 23.58; N, 3.44; P, 7.62. Found: C, 44.06; H, 4.99; Mo, 23.52; N, 3.46; P, 7.58. Mass spectrum (M_r = 407.26) ([ion], m/e for isotope ^{98}Mo (relative intensity)): $[MH]^+$, 410 (15.8%); $[M]^+$, 409 (94.5%); $[M - 2CO]^+$, 353 (100%); $[M - 2CO - H]^+$, 352 (64.5%).

(2,8-Dioxa-5-aza-1-phosphabicyclo[3.3.0]octane)chlorodicarbonyl(η^5-cyclopentadienyl)molybdenum(II) (6a). Ligand **1a** (233 mg, 1.75 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ (521 mg, 1.85 mmol) in 40 mL of THF. IR monitoring showed the reaction to be complete after 5 h at room temperature. The yellow-orange powder obtained by evaporation of the solvent was washed with 3 × 3 mL of ether and recrystallized at −30 °C from $CHCl_3/Et_2O$ (1/2), yielding 500 mg (74%) of small yellow crystals, mp 206 °C dec, soluble in the usual solvents except ether and hydrocarbons. Anal. Calcd for $C_{11}H_{13}ClMoNO_4P$: C, 34.25; H, 3.37; Cl, 9.21; Mo, 24.90; N, 3.63; P, 8.04. Found: C, 34.31; H, 3.31; Cl, 9.16; Mo, 24.83; N, 3.69; P, 8.16. Mass spectrum (M_r = 385.59; chemical ionization) ([ion], m/e for isotopes ^{98}Mo and ^{35}Cl (relative intensity)): $[MH]^+$, 338 (8%); $[M]^+$, 387 (19.9%); $[M - CO]^+$, 359 (3.9%); $[MH - Cl]^+$, 353 (15.6%); $[LH]^+$, 134 (100%).

(3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane)chlorodicarbonyl(η^5-cyclopentadienyl)molybdenum(II) (6b). Method a. Ligand **1b** (135.8 mg, 0.72 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ (200 mg, 0.71 mmol) in 20 mL of ether. The solution was stirred at room temperature, and an orange powder precipitated slowly. Infrared monitoring showed the reaction to be complete after 15 h. The powder was filtered, washed twice with 3 mL of ether, and recrystallized at −30 °C from $CHCl_3/Et_2O$ (1/2) to yield 250 mg (80%) of small ruby red crystals, mp 200 °C dec, soluble in the usual solvents except ether and hydrocarbons. Anal. Calcd for $C_{15}H_{21}ClMoNO_4P$: C, 40.77; H, 4.76; Cl, 8.04; Mo, 21.75; N, 3.18; P, 7.02. Found: C, 40.97; H, 4.80; Cl, 8.61; Mo, 21.76; N, 3.18; P, 7.25. Mass spectrum (M_r = 441.74; chemical ionization) ([ion], m/e for isotopes ^{98}Mo and ^{35}Cl (relative intensity)): $[MH]^+$, 445 (11.2%); $[M]^+$, 443 (7.8%); $[MH_2 - Cl]^+$, 410 (11.0%); $[M - Cl]^+$, 408 (9.8%); $[LH]^+$, 190 (100%).

Method b. Compound **5b** (**1b**) (150 mg, 0.37 mmol) was dissolved in 10 mL of CCl_4. The solution became red. ^1H NMR monitoring showed that the transformation was complete after 5 min at room temperature. Evaporation yielded 145 mg of an orange powder that was recrystallized at −30 °C from $CHCl_3$/EtO (1/2), yielding 130 mg (80%) of small ruby red crystals having the same physical and spectroscopic properties as those obtained by method a.

(Diethyl (dimethylamino)phosphonite)chlorodicarbonyl(η^5-cyclopentadienyl)molybdenum(II) (6c). The ligand $P(OEt)_2NMe_2$ (210 mg, 1.29 mmmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ (370 mg, 1.32 mmol) in 30 mL of THF. The solution was stirred for 10 h at room temperature; infrared monitoring then showed the reaction to be complete. After evaporation of the solvent, the orange powder was recyrstallized twice at −30 °C, first from $CHCl_3$/pentane (1/5), then from Et_2O/pentane (1/3), yielding 400 mg (75%) of small ruby red crystals,

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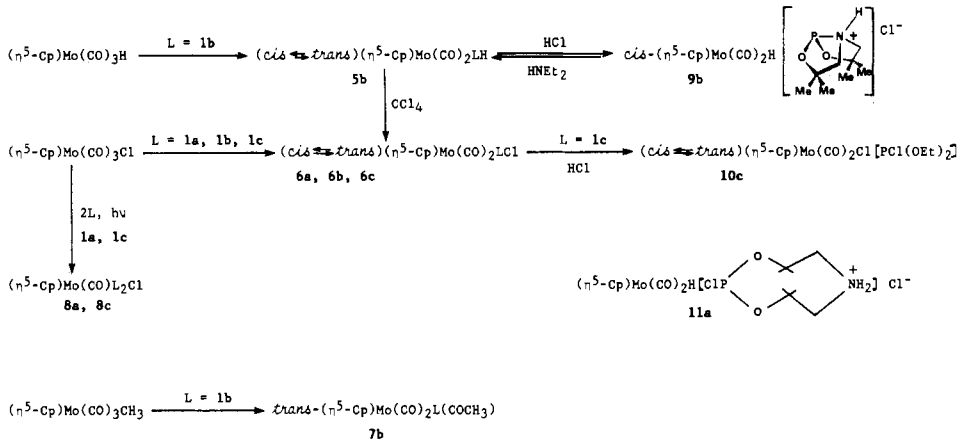
Scheme I



mp 117 °C, soluble in the usual solvents. Anal. Calcd for $C_{13}H_{21}ClMoNO_4P$: C, 37.54; H, 5.05; Cl, 8.54; Mo, 23.10; N, 3.37; P, 7.46. Found: C, 37.28; H, 5.07; Cl, 8.67; Mo, 21.59; N, 3.59; P, 7.41. Mass spectrum (M_r = 417.68; chemical ionization) ([ion], m/e for isotopes ^{98}Mo and ^{35}Cl (relative intensity)): $[MH]^+$, 420 (48.2%); $[M]^+$, 419 (100%); $[M - CO]^+$, 391 (10.3%); $[MH - Cl]^+$, 385 (11.4%); $[M - Cl]^+$, 384 (11.8%); $[M - NMe_2]^+$, 375 (28.7%); $[M - HNMe_2]^+$, 374 (55.1%); $[M - Cl - NMe_2]^+$, 341 (17%); $[M - Cl - HNMe_2]^+$, 340 (25.7%); $[LH]^+$, 166 (93.6%); $[L]^+$, 165 (7.4%).

(3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane)-acetyldicarbonyl(η^5-cyclopentadienyl)molybdenum(II) (7b). Ligand **1b** (412 mg, 2.18 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ (575 mg, 2.21 mmol) in 50 mL of hexane. The solution was boiled under reflux for 4 h; IR monitoring showed the reaction then to be complete. Upon cooling, a yellow-orange powder precipitated and was filtered. Evaporation of the solution yielded a yellow-orange powder, which has the same IR spectra as the precipitate. The crude reaction product (930 mg) was purified by column chromatography on neutral SiO_2 (Merck 60). The yellow fraction that was eluated with ether/toluene (4/10) yielded, after evaporation and recrystallization at −30 °C from toluene-/pentane (7/3), 805 mg (82%) of yellow parallelepipedic crystals, mp 135–137 °C dec, soluble in the usual solvents except hydrocarbons. Anal. Calcd for $C_{17}H_{24}MoNO_5P$: C, 45.43; H, 5.34; Mo, 21.38; N, 3.12; P, 6.90. Found: C, 45.49; H, 5.34; Mo, 20.46; N, 3.10; P, 6.91. Mass spectrum (M_r = 449.30; chemical ionization) ([ion], m/e for isotope ^{98}Mo (relative intensity)): $[MH]^+$, 452 (19.4%); $[M]^+$, 451 (22.5%); $[M - CO]^+$, 423 (31.2%); $[M - CH_2O]^+$, 421 (30.8%); $[M - 2CO]^+$, 395 (11.5%); $[M - CH_2O - CHO]^+$, 392 (43.4%); $[L - CH_2 - L]^+$, 391 (100%); $[M - 3CO]^+$, 367 (17.6%); $[LH]^+$, 190 (92%).

Bis(2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane)chlorocarbonyl-(η^5-cyclopentadienyl)molybdenum(II) (8a). Ligand **1a** (140 mg, 1.1 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ (140 mg, 0.50 mmol) in 60 mL of toluene that was irradiated by a HPK Philips lamp (125 W) for 8 h. IR monitoring then showed the reaction to be complete. After evaporation, the residue was washed with 3 mL of an $Et_2O/CHCl_3$ (2/1) mixture and recrystallized at −30 °C from pentane/$CHCl_3$ (2/3), yielding 160 mg (65%) of yellow crystals, dec pt 170 °C, soluble in most common solvents except ether and aliphatic hydrocarbons. Anal. Calcd for $C_{14}H_{21}ClMoN_2O_5P_2$: C, 34.27; H, 4.31; N, 5.71; P, 12.63. Found: C, 33.89; H, 4.98; N, 6.15; P, 13.32. Mass spectrum (M_r = 490.61; chemical ionization) ([ion], m/e for isotope ^{98}Mo (relative intensity)): $[MH]^+$, 493 (18.7%); $[M]^+$, 492 (34.6%); $[MH - Cl]^+$, 457 (11.8%); $[M - Cl - CO]^+$, 429 (20.5%); $[LH]^+$, 134 (100%).

Bis(diethyl (dimethylamino)phosphonite)chlorocarbonyl(η^5-cyclopentadienyl)molybdenum(II) (8c). Similar treatment of **1c** (130 mg, 0.80 mmol) and $(\eta^2\text{-}C_5H_5)Mo(CO)_3Cl$ (110 mg, 0.39 mmol) in 40 mL of toluene yielded, after two recrystallizations at −30 °C from pentane, 130 mg (61%) of small yellow crystals, mp 101 °C, soluble in the usual solvents. Anal. Calcd for $C_{18}H_{37}ClMoN_2O_5P_2$: C, 38.97; H, 6.72; Cl, 3.39; Mo, 17.29; N, 5.05; P, 11.16. Found: C, 38.91; H, 6.83; Cl, 6.23; Mo, 16.52; N, 4.80; P, 10.92. Mass spectrum (M_r = 555; chemical ionization) ([ion], m/e for isotope ^{98}Mo (relative intensity)): $[MH]^+$, 558 (1.2%); $[M^+]$, 557 (1.7%); $[M - Cl]^+$, 520 (1.1%); $[M - N(Me)_2]^+$, 513 (3.5%); $[M - N(Me)_2 - CO]^+$, 485 (1%); $[LH]^+$, 166 (100%).

(3,3,7,7-Tetramethyl-2,8-dioxa-5-azonia-1-phosphabicyclo[3.3.0]octane)hydridodicarbonyl(η^5-cyclopentadienyl)molybdenum(II) Chloride [(9b)(Cl^-)]. Method a. From 5b and an Excess of HCl. Gaseous HCl was bubbled into a solution of **5b** (350 mg, 0.86 mmol) in 30 mL of toluene for 15 min at −20 °C. The color of the solution changed from gold-yellow to pale yellow. Evaporation yielded a creamy white powder that was washed three times with 5 mL of pentane and dried under vacuum for 6 h, yielding 340 mg (90%) of (**9b**)(Cl^-), mp 135 °C dec, soluble in THF and sparingly soluble in ether and aliphatic or aromatic hydrocarbons. Anal. Calcd for $C_{15}H_{23}ClMoNO_4P$: C, 40.59; H, 5.19; Cl, 8.00; Mo, 21.65; N, 3.16; P, 6.99. Found: C, 39.80; H, 5.25; Cl, 7.85; Mo, 20.13; N, 3.21; P, 7.13. Mass spectrum (M_r = 443.72) ([ion], m/e for isotope ^{98}Mo and ^{35}Cl (relative intensity)): $[M - Cl]^+$, 410 (7%); $[M - HCl]^+$, 409 (41%); $[M - HCl - H]^+$, 408 (21%); $[M - HCl - 2CO]^+$, 353 (74%); $[M - HCl - H - 2CO]^+$, 352 (49%); $[C_5H_{10}NOP]^+$, 131 (100%).

Method b. From 5b and an Equimolar Amount of HCl. A dry 1.2 M solution of HCl in dry ether was prepared, 2.00 mL of which were added dropwise to a solution (0.86 g, 2.11 mol) of **5b** in 30 mL of toluene at −30 °C. The white precipitate that formed was stirred for 1 h, filtered, washed twice with 5 mL of toluene, and dried under vacuum for 12 h, giving 0.84 g (90%) of (**9b**)(Cl^-), identical with that prepared according to method a.

Trifluoromethanesulfonate Salt, (9b)($CF_3SO_3^-$). A solution of 133 mg (0.52 mmol) of $AgCF_3SO_3$ in 5 mL of MeCN was added to a solution of 230 mg (0.52 mmol) of (**9b**)(Cl^-) in 30 mL of MeCN. AgCl (70 mg) was filtered off after one night (95%) and the solution evaporated to leave a white air-sensitive powder soluble in CD_3CN and $PhNO_2$.

Deprotonation of (9b)(Cl^-). Diethylamine (0.43 mL, 4.5 mmol) was added dropwise to a suspension of (**9b**)(Cl^-) (1.82 g, 4.46 mmol) in 2 mL of toluene at −20 °C. The suspension turned into a pale yellow solution, which was filtered on a small column of neutral silica (Merck 60, 4 g). The column was first washed with 5 mL of toluene and 10 mL of pentane, and the effluents were cooled to −20 °C, allowing the yellow crystals (1.33 g, 80% yield) of the regenerated **5b** to precipitate. The column was then washed with 3 × 10 mL of ethanol, which after evaporation gave H_2NEt_2Cl (380 mg, 84.5%). Both products were identified with authentic samples. A similar experiment using triethylamine gave comparable results.

(Diethyl chlorophosphonite)chlorodicarbonyl(η^5-cyclopentadienyl)molybdenum(II) (10). A solution of **6c** (180 mg, 0.43 mmol) in 20 mL of hexane was treated with HCl gas for 10 min. The color of the solution changed from red to orange, and a brown oil precipitated. After filtration, the oil was washed twice with 2 mL of THF, yielding a creamy-white powder identified as $[Me_2NH_2]Cl$ (yield 88%) by ^1H NMR spectroscopy ($\delta(CH_3)$ = 2.73 (s); $\delta(H)$ = 9.47 (s). Evaporation of the solvent followed by two recrystallizations at −30 °C from pentane yielded 125 mg (71%) of small red crystals (mp 54 °C) soluble in the common solvents. Anal. Calcd for $C_{11}H_{15}Cl_2MoO_4P$: C, 32.30; H, 3.70; Mo, 23.45; P, 7.57. Found: C, 32.55; H, 3.76; Mo, 23.46; P, 7.65. Mass spectrum (M_r = 409.06; chemical ionization) ([ion], m/e for isotopes ^{98}Mo and ^{35}Cl (relative intensity)): $[M + NH_4]^+$, 428 (50.0%); $[M + NH_3]^+$, 427 (100%); M^+, 410 (7.9%); $[M + NH_3 - Cl]$, 392 (15.3%); $[M + NH_3 - HCl]$, 391 (49.3%).

Results and Discussion

Adducts of (η^5-Cyclopentadienyl)molybdenum(II) Carbonyl Hydride, Chloride, and Acetylate with the Aminophosphanes 1. Increased π-Accepting Character of the Bicyclic Ligands with Respect to Their Nonconstrained Analogue. The bicyclic aminophosphane **1b**, when allowed to react in equimolar proportions with $CpMo(CO)_3X$, where X = H or Cl, readily displaces one CO to give the monosubstituted P-coordinted adducts **5b** and **6b**

(Scheme I; Tables I and II). Similar behavior was observed when the nonmethylated, less stable ligand **1a** and the noncyclic $(EtO)_2PNMe_2$ ligand **1c** were allowed to react with $CpMo(CO)_2Cl$, yielding **6b** and **6c**, respectively. With $CpMo(CO)_3CH_3$, the coordination is accompanied by the insertion of a CO group into the $Mo-CH_3$ bond, as observed with other phosphanes or phosphites,[14] to give **7b**. **6b** was also obtained by the action of CCl_4 on **5b**; in this case, ^1H monitoring shows the progressive disappearance of the hydride proton signal at high field and the concomitant appearance of the $CHCl_3$ singlet at 7.25 ppm.

All five monosubstituted adducts were isolated in good yields. They are thermally stable but air sensitive, especially **6a**, which is highly oxygen sensitive. It is noteworthy that **6a** is thermally stable (dec pt >200 °C) in contrast to the free ligand, which tends to polymerize already at room temperature. Their composition was checked by elemental analysis and mass spectroscopy. A molar conductance measurement performed on **6b** proved it to be covalent ($\Lambda = 4.3\ \Omega^{-1}\ cm^2 \cdot mol^{-1}$ in CH_3CN).

That coordination occurs through phosphorus is asserted by the downfield shift of the ^{31}P NMR signal (average 52 ppm, including that for **6c**) and by its coupling with the hydride proton in the case of **5b** and with the cyclopentadienyl protons in the case of the trans isomers (vide infra) (Table I).

All adducts showed the expected two $\nu(CO)$ absorptions in the infrared spectrum (Table II); compound **7b** shows in addition to those at 1954 and 1878 cm^{-1}, a $\nu(CO)$ vibration at 1634 cm^{-1} assigned to the acyl group. It is believed that all retain the square-pyramidal structure usually adopted by cyclopentadienylmolybdenum(II) derivatives.[15] The presence of the two isomers was indeed evidenced here by ^1H and ^{31}P NMR. For the hydride complexes **5b** the cis/trans interconversion is rapid. At room temperature the NMR spectrum shows a singlet for the cyclopentadienyl protons and a doublet for the hydride protons (average $^2J_{P-H} = 50.7$ Hz), while at −40 °C two sets of signals of different intensities appear. Similarly, the doublet at 219.9 ppm observed at 25 °C in the proton-coupled ^{31}P NMR spectrum splits at −40 °C into two doublets of quintuplet located at 216.5 and 222.0 ppm. These were respectively assigned to the cis and trans isomers (in 70/30 ratio) on the basis of the $^2J_{P-H}$ values, the larger coupling, 61 Hz, being assigned to the cis isomer and the smaller one, 26 Hz, to the trans isomer.[16] The former isomer also exhibits a coupling between phosphorus and the protons located on the carbon atoms α to nitrogen ($^3J_{P-H} = 12$ Hz). A value of $\Delta G^{\ddagger} = 12.4 \pm 0.5$ kcal·mol^{-1} for the cis/trans interconversion was calculated by the slow-exchange method.[17] This is comparable to those obtained for other $CpMo(CO)_2LH$ adducts, where L = $PhP(OMe)_2$[16d] and $PhP(OCH_2CH_2)_2NH$.[8c] The interconversion is much slower for the molybdenum chloride adduct **6b**, which already exhibits distinct ^1H and ^{31}P NMR signals for the two isomers even at room temperature. The cis/trans ratio was found to depend on the solvent (94/6 in toluene and 83/17 in $CHCl_3$ at 25 °C by ^{31}P NMR). Similar observations were made in the case of **6a** and **6c**.

Interestingly, the infrared spectra of **6b**, measured on KBr pellets, exhibit different $\nu(CO)$ vibration frequencies, depending on whether the product is recrystallized from $CHCl_3/Et_2O$ (1970 (vs), 1858 (vs) cm^{-1}) or from toluene (1992 (s), 1900 (vs) cm^{-1}). Both samples, when redissolved in $CHCl_3$, give identical infrared spectra for the two solutions (1980 (vs), 1900 (vs) cm^{-1}). A similar observation was made in the case of **6a**. Whether they correspond to the cis and trans isomers or to adducts in which the ligand would adopt different conformations within the metal's coordination sphere, remains undetermined. The isolation of only one isomer in the solid state has previously been observed for a similar compound.[15c]

The NMR spectra of the acyl derivative **7b** exhibited only one set of signals and did not show any change from ambient temperature to −40 °C. The detection of a $^3J_{H-P}$ coupling of 0.9 Hz points to the presence of the trans isomer.

Most significant is the increase in $\nu(CO)$ stretching frequencies (Table II) observed when going from the nonconstrained ligand **1c** to the tetramethylated bicyclic **1b** and then to the less sterically hindered ligand **1a**: this is the order in which one would expect the angles at nitrogen and, concomitantly, the efficacy of the $N(p_\pi)-P(d_\pi)$ interaction to decreased, with as a result a compensatory increase in π-accepting character of the phosphorus toward the transition metal.

The substitution of a second carbonyl group of $CpMo(CO)_3Cl$ was not observed in the presence of a threefold excess of **1a** after 8 days at room temperature or 48 h at reflux in THF but occurred in a matter of hours at room temperature under photochemical activation. Both **1a** and **1c** then gave disubstituted complexes in good yields. Their formulation is attested by their elemental analysis, mass spectra, and the presence of a single $\nu(CO)$ vibration in the IR ($CHCl_3$). The frequency of this vibration is again significantly higher for the **1a** adduct (1840 cm^{-1}) than for its noncyclic analogue (1799 cm^{-1}). In both cases the ^{31}P NMR spectra presented single signals, indicating a trans arrangement of the two phosphane ligands. This is corroborated by the presence of only one signal for the cyclopentadienyl protons. The substitution of more than two carbonyls was not observed.

Basicity of the Nitrogen Atom of Ligand 1b. Protonation of the Nitrogen vs. P–N Bond Opening. No example of a compound with a protonated phosphorus-bound nitrogen atom appears to have been reported so far. The haloacids as a rule cleave the P–N bond of aminophosphanes, aminophosphane oxides, and related compounds to give the corresponding halophosphane derivatives together with ammonium halides.[10] Coordination of the phosphorus atom to transition metals does not change the issue of the reaction.[11] It is therefore noteworthy that complex **5b** containing the bicyclic ligand **1b**, by contrast, led to isolable and unexpectedly stable (dec pt 135 °C) phosphorammonium salts **9b** with Cl^- or $CF_3SO_3^-$ as the anions. This appears to be the first example of protonation of a phosphorus-bound nitrogen atom with preservation of the P–N bond.[18]

When gaseous HCl is bubbled through a solution of **5b** in toluene at −20 °C, (**9b**)(Cl^-) is precipitated and can be isolated in 90% yield. Composition of (**9b**)(Cl^-) was ascertained by elemental analysis and mass spectrometry. The use of a calibrated HCl solution in ether showed that only 1 molar equiv of HCl is required to complete the reaction, whereas the P–N cleavage reaction would require 2 molar equiv to give the ammonium salt of the monocyclic open compound **11**. The anion was readily exchanged under the action of $AgCF_3SO_3$, and the ionic nature of the resulting species was established by conductivity measurements (the chloride was unstable in nitrobenzene). **9b** could be deprotonated under the action of 1 equiv of diethylamine to restore adduct **5b**, which was isolated in 80% yield along with H_2NEt_2Cl. A similar behavior was observed when **6b** was treated with 1 equiv of HCl, and the reaction product could be converted back to **6b** under the action of diethylamine.

The preservation of the P–N bond is also established by the ^1H NMR spectrum of **9b** (CD_3CN), which exhibits an eight-line phosphorus-coupled AB system for the CH_2 groups of the five-membered rings ($\delta_A = 3.82$, $\delta_B = 3.44$; $J_{AB} = 13$, $^1/_2(J_{H_AP} + J_{H_BP}) = 0.4$ Hz), a system analogous to that found for the free ligands,

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with only slight differences in chemical shift and coupling constants ($\delta_A = 3.08$, $\delta_B = 2.75$; $J_{AB} = 12$, $^1/_2(J_{H_AP} + J_{H_BP}) = 0.3$ Hz in C_6D_6). A broad signal, at 11.55 ppm, was assigned to the ammonium proton. No changes in the spectra were observed down to −80 °C. The retention of the bicyclic structure is further ascertained by the close resemblance of the mass and infrared spectra of **9b** and **5b**.

By contrast, when the adduct of the noncyclic ligand **1c** was treated with HCl in comparable experimental conditions, it readily led (with 2 equiv of HCl) to the chlorophosphane adduct $CpMo(CO)_2[PCl(OEt)_2]Cl$ (**10c**) and dimethylammonium chloride, which were isolated in 70 and 90% yields, respectively, showing that the usual P–N bond cleavage reaction takes place in this case. Adduct **10c** was characterized by its elemental analysis and mass, infrared, ^{31}P NMR, and ^1H NMR spectra (Tables I and II).

These experiments establish that a phosphorus-bound nitrogen atom can display definite basicity when incorporated in constrained structures that require the nitrogen atom to adopt a pyramidal geometry.

Registry No. **1a**, 65693-26-7; **1b**, 75194-94-4; **1c**, 2632-87-3; *cis*-**5b**, 97466-39-2; *trans*-**5b**, 97466-40-5; *cis*-**6a**, 97416-61-0; *trans*-**6a**, 97466-41-6; *cis*-**6b**, 97416-62-1; *trans*-**6b**, 97466-42-7; *cis*-**6c**, 97416-63-2; *trans*-**6c**, 97466-43-8; *trans*-**7b**, 97416-64-3; *trans*-**8a**, 97416-65-4; *trans*-**8c**, 97416-66-5; (**9b**)(Cl^-), 97548-95-3; (**9b**)($CF_3SO_3^-$), 97548-96-4; *cis*-**10c**, 97416-67-6; *trans*-**10c**, 97466-44-9; (η^5-C_5H_5)Mo(CO)$_3$H, 12176-06-6; (η^5-C_5H_5)Mo(CO)$_3$Cl, 12128-23-3; (η^5-C_5H_5)Mo(CO)$_3$CH$_3$, 12082-25-6.

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Metal Complexes of Tetrapyrrole Ligands. 36.[1] Proton NMR Spectra of Cobalt(II) 5,15-Dialkyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrins (Decaalkylporphodimethenes)

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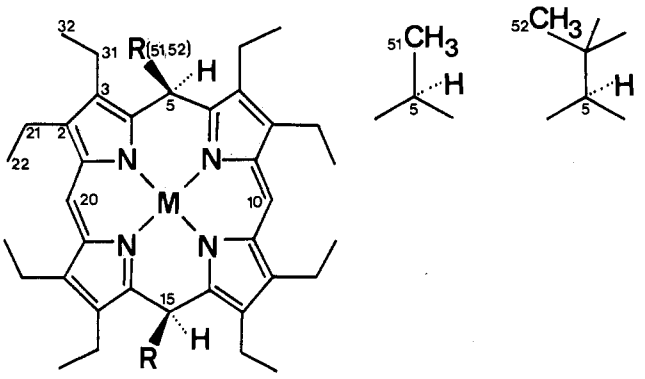
A series of four square-planar cobalt(II) 5,15-dialkyloctaethylporphodimethenes, $Co(OEPR_2)$, have been synthesized and their ^1H NMR spectra interpreted. All complexes were isolated as the stereoisomer in which the alkyl groups, R, are syn-axial. The complexes are low spin and have ^1H NMR spectra consistent with a ^2A $(d_{z^2})^1$ ground state. The isotropic shifts are predominantly dipolar in origin and exhibit a linear $1/T$ dependence with non-zero intercept. The line widths (20–440 Hz) are determined exclusively by a dipolar relaxation mechanism with a short correlation time, $\tau_c = 2 \times 10^{-12}$ s. From an analysis of the relative isotropic shifts and relative line widths, the geometry of $Co(OEPR_2)$ in solution appears to be substantially nonplanar with both folding of the macrocycle and ruffling of the pyrrole rings. This is consistent with the known solid-state structures of metalloporphodimethenes.

During their work on the oxidation of uroporphyrinogens to uroporphyrins with iodine, Mauzerall and Granick[3] discussed the occurrence of porphomethenes (5,10,15,20-tetrahydroporphyrins) and porphodimethenes (5,15-dihydroporphyrins) as air-labile intermediates. Air-labile metal complexes of porphodimethenes were later found in photoreductions of zinc porphyrins[4] and chemical reductions of zinc or aluminum octaethylporphyrins.[5–7] In order to prepare these reduced tetrapyrrole complexes more readily, the reductive alkylation of metal complexes of octaethylporphyrin (OEP)[8] was developed.[1,6,8] This furnishes air-stable metal complexes of 5,15-dialkyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrins (decaalkylporphodimethenes) of the general formula $M(OEPR_2)$ as shown in structures **1–4**.[9] While the direct reductive alkylation of zinc tetra-



1: $Co(OEPMe_2)$, R = CH_3
2: $Co(OEPEt_2)$, R = C_2H_5
3: $Co(OEPPr_2)$, R = i-C_3H_7
4: $Co(OEPBu_2)$, R = t-C_4H_9

phenylporphyrin, Zn(TPP),[10] does not produce the corresponding porphodimethene, a reductive addition of two allyl groups at 5,15-C of Fe(TPP) has been accomplished by Mansuy et al.[11]

According to the ^1H NMR data[7,10b] and several X-ray structure determinations by Scheidt et al.,[12] the alkyl groups introduced

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(8) Abbreviations used: $(OEP)^{2-}$, $(TPP)^{2-}$, $(TTP)^{2-}$, $(OEPR_2)^{2-}$, the dianions of octaethylporphyrin, *meso*-tetraphenylporphyrin, *meso*-tetra-*p*-tolylporphyrin, and 5,15-dialkyloctaethylporphodimethene, respectively; L, axial ligands; Im, imidazole; pip, piperidine.
(9) The numbering scheme applied in the formula fulfills the IUPAC numbering rules for the C atoms of the porphyrin skeleton. The second digit of the numbers 21, 22, 31, 32, 51, and 52 defines the first or second carbon in a side chain extending from the porphyrin positions 2, 3, 5, and the corresponding symmetry-related positions. 21,31-H are jointly referred to as α-CH_2 and 22,32-H as β-CH_3 protons.
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