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Synthesis and Spectral Properties of Metal Carbonyl Derivatives of the Tetrabasic, Nonchelating Phosphatriazaadamantane Ligand

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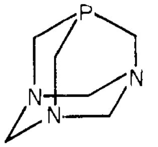
Although the inorganic chemistry of tetraazaadamantane ($N_4(CH_2)_6$, also known as hexamine or urotropin) has commanded a good deal of attention with respect to its reactions with main group or transition metal salts,[2] spectral properties of derivatives thus formed are in general not available. Similarly, low-valent organometallic complexes such as η^5-$C_5H_5Mo(CO)_2[N_4(CH_2)_6]$[3] or $Mo(CO)_5[N_4(CH_2)_6]$[4] have been prepared but not extensively studied. The recent synthesis[5] of phosphatriazaadamantane, PTA, prompted an investigation into the complexing properties of this novel tetrabasic, nonchelating ligand. In view of the fact that metal carbonyl moieties are known to bond to both N and P donor ligands, derivatives of the formulas $M(CO)_5PTA$ (M = Cr, Mo, W) and $Fe(CO)_4PTA$ as well as the N-methylated $[M(CO)_5PN_2(CH_2)_6NCH_3]^+I^-$ were prepared. For comparison, ir and nmr spectral data were also measured for the tetraazaadamantane complex $Mo(CO)_5[N_4(CH_2)_6]$.



PTA

Experimental Section

Materials. Phosphatriazaadamantane and tetraazaadamantane were prepared as described in the literature.[5,6] Bis(2-methoxyethyl) ether (diglyme), purified by reflux over and distillation from sodium under N_2, was used as solvent for the thermal reactions. Other solvents and chemicals were reagent grade and used without further purification.

Procedure. Stoichiometric amounts (6.37 mmol) of PTA and $M(CO)_6$ or $Fe(CO)_5$ were allowed to react in 15–20 ml of diglyme and refluxed under N_2 for 2–3 hr. Upon removal of solvent *in vacuo* a yellow to white residue was obtained, was washed with water, and was recrystallized from boiling hexane. Any excess $M(CO)_6$ was removed by sublimation at 1 mm and 40–50°. $Cr(CO)_5PTA$ was found to sublime slowly, over a period of days, at 90°. *Anal.* (Galbraith Laboratories) Calcd for $Cr(CO)_5[PN_3(CH_2)_6]$: C, 37.83; H, 3.46. Found: C, 37.67; H, 3.45. Calcd for $Mo(CO)_5[PN_3(CH_2)_6]$: C, 33.60; H, 3.08; mol wt 393. Found: C, 33.85; H, 3.11; mol wt 410. Calcd for $W(CO)_5[PN_3(CH_2)_6]$ C, 27.46; H, 2.51. Found: C, 27.24; H, 2.64. Calcd for $Fe(CO)_4[PN_3(CH_2)_6]$: C, 36.95; H, 3.72. Found: C, 37.23; H, 3.53. In all cases yields were approximately 50%.

Pentacarbonyl(tetraazaadamantane)molybdenum was obtained by allowing $Mo(CO)_6$ and $N_4(CH_2)_6$ to react in refluxing methylcyclohexane. A yellow crystalline precipitate was obtained on cooling, was washed with water, and was recrystallized from hexane.

Alternatively the $M(CO)_5L$ (L = PTA, $N_4(CH_2)_6$) complexes could be prepared by treating L with $M(CO)_5THF$, produced photochemically[7] in THF.

Infrared spectra were obtained on a Perkin-Elmer 521 spectrophotometer, calibrated in the CO stretching region with CO and H_2O vapor. A Jeolco MH-100 was used to obtain the proton nmr resonances; ^{31}P resonances were measured on a Jeolco C-60 HL spectrometer, equipped with a 24-MHz radiofrequency unit.

Results and Discussion

Air-stable crystalline solids result from reaction of PTA and excess $M(CO)_6$ (M = Cr, Mo, W) or $Fe(CO)_5$ in refluxing dry diglyme. Alternatively the group VI derivatives could be prepared by the photochemical synthesis of $M(CO)_5THF$ complex and subsequent thermal (25°) reaction with PTA *in situ*. Products obtained by this method are identical with those obtained by the thermal rupture of an M–CO bond; yields were also similar.

Spectral properties of the complexes are found in Table I. The infrared spectra for $M(CO)_5PTA$ complexes measured in the CO stretching frequency region show a pattern typical of monosubstituted octahedral metal carbonyl complexes, with frequencies very similar to those of phosphine-substituted complexes, the definitive feature being the position of the $A_1^{(1)}$ band with respect to the E band. $LM(CO)_5$ complexes in which L is a phosphorus donor generally exhibit ν_{CO} spectra in which the $A_1^{(1)}$ bands are higher in energy from the E mode, whereas if L is a nitrogen donor, the $A_1^{(1)}$ band is lower in energy from the E.[8] The latter is the case for $Mo(CO)_5N_4(CH_2)_6$. The ν_{CO} ir spectrum observed for $Fe(CO)_4PTA$ is typical of axially substituted trigonal-bipyramidal iron carbonyl complexes.[9] C–K force constant values[10] for the PTA complexes are similar to those calculated for analogous carbonyl complexes containing phosphorus donor ligands[8] or, in the case of $MO(CO)_5[N_4(CH_2)_6]$, nitrogen donor ligands.[11]

The ^1H nmr data also suggest PTA to be phosphorus-bound to its metal carbonyl derivatives. Uncomplexed PTA in acetone exhibits two resonances, integrating 1:1, at δ 4.50 and 3.97 ppm. The latter resonance is split by 10 Hz and is assigned to the P–CH_2–N protons. The methylene protons adjacent to P in the metal carbonyl PTA complexes show both a resonance shift downfield from noncomplexed PTA as well as

Table I. Carbonyl Stretching Frequency Data, Cotton–Kraihanzel Force Constants, Nmr Parameters, and Physical Properties for Metal Carbonyl Complexes of Phosphatriazaadamantane and Tetraazaadamantane

	$Cr(CO)_5PTA$	$Mo(CO)_5PTA$	$W(CO)_5PTA$	$Fe(CO)_4PTA$	$Mo(CO)_5[N_4(CH_2)_6]$
		ν_{CO},[a] cm^{-1}			
$A_1^{(2)}$	2062 w	2070 w	2070 w	2052 w	2070.5 w
^{13}C	2056 vw	2063 vw	2062 vw		
$A_1^{(1)}$	1959 m	1958 m	1954 m	1982 w	1939.3 s
E	1943 s	1948 s	1943 s	1943 s	1927.1 m
^{13}C	1915 vw	1918 vw	1913 vw	1908 vw	
		C–K Force Constants[b]			
k_{ax}	15.73	15.71	15.73	16.29	15.20
k_{eq}	15.82	15.91	15.82	15.68	15.84
		δ,[c] ppm			
$P(CH_2)N$ (J_{P-H})	4.25 (1.8 Hz)	4.28 (2.3 Hz)	4.31 (<1 Hz)	4.30 (0)	4.94[d]
$N(CH_2)N$	4.56 s	4.60 s	4.62 s	4.62	4.58 4.64 [e]
		Color and Mp, °C			
	Light yellow	Off-white	Yellow	Yellow	Yellow
	132.5	122	143	157–159	177–180 dec

[a] Measured in hexane solution; 1-mm NaCl cells. [b] References 8 and 10. [c] Acetone-d_6 solution; internal TMS = 0 standard. [d] Assigned to Mo–N–CH_2N; integrates to 6 protons. [e] Assigned to N–CH_2N; integrates to 3 + 3 protons.

a distinct reduction in P–H coupling constant. Assuming the ligand to be P-bound, the downfield shift is expected as electron density is removed upon coordination. The P–H coupling constant change will be further explored in a subsequent work. The ^{31}P nmr spectrum for a H_2O solution of PTA displays a septet, centered at +100 ppm relative to 85% H_3PO_4 with J_{P-H} = 9.5 Hz. A partially resolved resonance centered at +58 ppm with an approximately 12-Hz spread is observed in the ^{31}P spectrum of $Mo(CO)_5PTA$ in DMSO-d_6. These ^{31}P resonance data agree with the correlation observed by Shaw, *et al.*, between the ^{31}P chemical shift of free tertiary phosphines and changes in ^{31}P chemical shift upon coordination.[12]

The ^1H nmr spectrum of tetraazaadamantane in acetone-d_6 consists of a sharp singlet at 4.58 ppm. Upon coordination to $Mo(CO)_5$ three resonances are observed. The low-field resonance (δ 4.94, 6 protons) is assigned to methylene protons adjacent to the coordinated nitrogen; the higher field set of two resonances, integrating to 3 protons each, is assigned to protons of methylenes bridging the uncomplexed nitrogens, the nonequivalency of the axial and equatorial hydrogens in the cyclohexane-like base of the ligand accounting for the resolution. This resolution is solvent dependent; for example, the ^1H nmr of $Mo(CO)_5[N_4(CH_2)_6]$ in $CDCl_3$ exhibits only two sharp resonances, at 4.76 and 4.55 ppm, integrating to 6 protons each. On the other hand resolution of high-field N–CH_2–N in $M(CO)_5PTA$ (M = Cr, Mo) complexes is observed in DMSO-d_6. A more complete study of solvent effects on nmr spectra of these and other PTA derivatives is forthcoming from our laboratories.

Alkylated derivatives such as $(CO)_5WPTAMe^+I^-$ may be prepared either by reaction of $W(CO)_5PTA$ with MeI in warm acetone solution or by reaction of $(CO)_5W(THF)$ complex with the N-alkylated $PTAMe^+I^-$ salt.[5] The ν_{CO} ir spectrum of this compound is very similar to that of the nonalkylated tungsten derivative in THF with frequencies of 2075 (w) and 1950 (br, s) cm^{-1}. The ^1H nmr spectrum is complex and is open to alternate interpretation based on assumption of $PTAMe^+I^-$ being N- or P–M-coordinated. This complex is less stable thermally than its nonalkylated congener.

Main-group metal organic reagents (RM′) were found to add to the carbonyl group cis to PTA in $M(CO)_5PTA$ yielding *cis*-$M(CO)_4(PTA)C(O)R^-M'^+$ (R = $PhCH_2$, M′ = $MgCl^+$; R = Ph, M′ = Li). The rate of addition of $PhCH_2MgCl$ (0.167 *M*) to $Cr(CO)_5PTA$ (0.0087 *M*) was followed at 25° in THF and the pseudo-first-order rate constant determined to be 1.0 (±0.1) × 10^{-3} sec^{-1}. This value is similar to that observed for reaction of $Me_3PCr(CO)_5$ with $PhCH_2MgCl$ and, on basis of our earlier correlation of rates of nucleophilic addition to carbonyl carbon atoms and steric requirements of ligands cis to the addition site,[13] would corroborate the expected very small steric requirement of PTA, on the order of PMe_3. As estimated from molecular models, the Cr–PTA ligand cone angle is 115 ± 5°.[14]

Attempts to alkylate these acylate anions, *cis*-$M(CO)_4(PTA)C(O)R^-M'^+$, with $MeOSO_2F$ or $Et_3O^+BF_4^-$ led to inseparable mixtures of carbene complex, *cis*-$M(CO)_4(PTA)C(OR')R$,[15] and alkylated PTA complexes.

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Registry No. $Cr(CO)_5PTA$, 54340-46-4; $Mo(CO)_5PTA$, 54340-47-5; $W(CO)_5PTA$, 54340-48-6; $Fe(CO)_4PTA$, 54340-49-7; $Mo(CO)_5[N_4(CH_2)_6]$, 54340-45-3; $(CO)_5WPTAMe^+I^-$, 54340-50-0; $PhCH_2MgCl$, 6921-34-2; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Fe(CO)_5$, 13463-40-6.

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