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Syntheses and structures of [Mo(CO)$_3$(TPA)$_3$] and [Mo(CO)$_3$(ETPB)$_3$]. A structural and spectroscopic correlation

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Abstract—Molybdenum tricarbonyl complexes of the type [Mo(CO)$_3$L$_3$] (where L = 1,3,5-triaza-7-phosphaadamantane [TPA] or 4-ethyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane [ETPB] have been synthesized and characterized by IR, ^{1}H, ^{31}P and ^{95}Mo NMR spectroscopies and single crystal X-ray diffraction methods. The X-ray structural determinations are correlated with the observed spectroscopic data. The average Mo—P bond distance in [Mo(CO)$_3$(TPA)$_3$] [2.489(9) Å] is longer than in the corresponding [Mo(CO)$_3$(ETPB)$_3$] complex [2.428(5) Å] which is consistent with weaker π-acceptor ability for the cyclic aliphatic TPA ligand compared to the cage phosphite ETPB ligand. © 1997 Elsevier Science Ltd

Keywords: molybdenum carbonyl phosphine complexes; crystal structures; ^{95}Mo NMR.

The ^{95}Mo chemical shifts of [Mo(CO)$_{6-n}$(L)$_n$] (n = 1, 2, or 3, L = phosphite or phosphine) complexes directly reflect the nature of M—P bonding [1]. In general, it is established that the chemical shift undergoes downfield shifts with decreased σ bonding and/or π bonding and increased steric hindrance. We have undertaken structural and spectroscopic correlations of these complexes to quantity these well documented qualitative NMR observations. It is already clear that high field δ(^{95}Mo) values and shorter Mo—P bonds are observed for all strong π bonding phosphite ligands whereas downfield δ(^{95}Mo) and longer Mo—P bonds are found for all weak π bonding phosphine ligands [2]. The 1,3,5-triaza-7-phosphaadamantane [TPA] (previously called PTA) and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane [ETPB] are the smallest known phosphine and phosphite (cone angles of 102 and 101°, respectively for TPA and ETPB) [3]. Hence, the steric effects on δ(^{95}Mo) in the complexes [Mo(CO)$_{6-n}$(L)$_n$] (L = TPA or ETPB) might be expected to be minimized and the observed δ(^{95}Mo) in these complexes should thus mainly depend on the δ- and π-acceptor nature of these ligands. In continuation of our studies on the structural and spectroscopic correlations of molybdenum-phosphine/phosphite complexes [2], we report here the structural–spectroscopic comparison of the two complexes [Mo(CO)$_3$(TPA)$_3$] (**1**) and [Mo(CO)$_3$(ETPB)$_3$] (**2**). The former complex was not isolated in our earlier attempt at its synthesis [4]. The relatively few X-ray structural determinations for Group 6 metal *fac*-M(CO)$_3$ P$_3$ fragments were summarized in our recent report on *fac*-Mo(CO)$_3$(P(OC$_6$H$_5$)$_3$)$_3$) (**3**) [2c].

EXPERIMENTAL

Hexacarbonymolybdenum [Mo(CO)$_6$] (Aldrich, U.S.A.) and 4-ethyl,2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane (Strem Chemicals, U.S.A.) were obtained from the given commercial sources. The TPA ligand [5] and [Mo(CO)$_3$(mesitylene)] [6] were prepared according to the reported methods. All the solvents were dried prior to use. The IR spectra were recorded on a Nicolet 20DXC FTIR instrument using Nujol mulls between KBr plates (4000–400 cm^{-1}). The ^{31}P NMR spectra were recorded on a Varian Unity-400 instrument operating at 162.1 MHz and the ^{1}H NMR spectra were recorded on a Varian Gemini-200 instrument. The chemical shifts are relative to the external 85% H$_3$PO$_4$ peak for ^{31}P and internal chloroform peak (δ 7.26 ppm) for ^{1}H NMR spectra.

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The ^{95}Mo NMR spectral data were recorded previously using 2M Na_2MoO_4 in aqueous alkaline solution as the external standard [2f,4].

Preparation of [Mo(CO)$_3$(TPA)$_3$] (**1**)

To a dichloromethane solution (20 cm^3) of [Mo (CO)$_3$(mesitylene)] (120 mg, 0.4 mmol) TPA (189 mg, 1.20 mmol in methanol) was added and the solution stirred for 5 h under a nitrogen atmosphere. Following solvent removal *in vacuo*, the residue was recrystallized from dichloromethane/methanol solution giving crystals of the title compound. Yield 220 mg, 84.5%. M.p., 230(dec); IR(Nujol, ν_{co}, cm^{-1}): 1930, 1840; ^{31}P NMR(CDCl$_3$, δ in ppm): -51.47, ^1J (Mo-P) = 127 Hz; ^{1}H NMR(CDCl$_3$): 4.6–4.8(br).

Preparation of [Mo(CO)$_3$(ETPB)$_3$] (**2**)

To a dichloromethane solution (20 cm^3) of [Mo (CO)$_3$(mesitylene)] (120 mg, 0.40 mmol) solid ETPB (195 mg, 1.20 mmol) was added and the solution was stirred for 3 h. The solvent was removed *in vacuo*, the residue extracted with toluene and the solution filtered. The addition of heptane to the filtrate yielded a colorless product of the title compound, which was filtered, washed with heptane and dried. The product was recrystallized from a toluene/heptane solution. Yield, 200 mg, 75%. M.p, 175°C; IR (Nujol, ν_{co}, cm^{-1}): 1980, 1895; ^{31}P (CDCl$_3$, δ in ppm): 142.9, ^{1}J(Mo—P) = 229 Hz; ^{1}H NMR(CDCl$_3$): 4.1 (OCH$_2$, 18H), 1.131 (q, —CH$_2$—, ^3J(HH) = 7.6 Hz, 6H), 0.763 (t, CH$_3$, ^1J(HH) = 8 Hz, 9H).

Crystallography

Details of data collection, structure solution and refinement for (**1**) and (**2**) are summarised in Table 1. Both crystals suffered considerable decay in the X-ray beam and this was allowed for by appropriate scaling. Compound (**1**) has two independent molecules in the asymmetric unit; both have similar stereochemistry. For compound (**2**) it soon became apparent that there were two disordered toluene molecules in the asymmetric unit, one at the origin and one in a general position occupying what would otherwise have been voids in the crystal lattice. Attempts at modelling these disordered solvent molecules were not successful and prior to the final refinement cycles, their contributions to the structure factors were removed using the SQUEEZE option in PLATON [9]. In (**2**), each ETBP ligand is disordered over two sites (by rotation about a P $\cdots$ C axis) and this was allowed for using suitable constraints in the SHELXL93 [8] refinement. Because of the decay during the data collections for (**1**) and (**2**) (and the disorder of the ligands in (**2**)) the analyses are not of high accuracy, but they do serve to establish the structures unequivocally. Only the Mo, P and carbonyl atoms were allowed anisotropic displacement parameters, all other C, N and O atoms were refined isotropically. H atoms were positioned geometrically and treated as riding atoms. The final positional and displacement parameters, structure factors, full list of bond lengths and angles involving all non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre and are also available from the authors in CIF format.

RESULTS AND DISCUSSION

The reaction of [Mo(CO)$_3$(mesitylene)] with TPA or ETPB in dichloromethane/methanol or dichloromethane yielded the mononuclear complexes [Mo(CO)$_3$L$_3$] (L = TPA or ETPB). The IR spectra show that the complexes exist exclusively in the tricarbonyl form. The observed ν_{co} frequencies for complex (**1**) [1930, 1840 cm^{-1}] are considerably lower than those for (**2**) [1980, 1895 cm^{-1}]. This is undoubtedly due to the stronger metal-to-carbonyl back bonding in molecule (**1**) compared with that in (**2**). The ^{31}P NMR spectra of the complexes display single resonances with six molybdenum satellites ($I = 5/2$ for Mo), indicating that the complexes exist exclusively in the facial-isomeric form (since for the mer-isomer, two ^{31}P signals are expected).

The ORTEP [10] plots of one of the two molecules of (**1**) and that of (**2**) are shown in Figs 1 and 2, while selected dimensions for (1) and (2) are given in Table 2. The structures have the expected facial octahedral coordination of Mo. The mean Mo—C(carbonyl) and carbonyl CO distances in molecule (**1**) [1.964(8), 1.160(14) Å] are not significantly different from the mean values in (**2**) [1.98(2), 1.153(12) Å] and are within the accepted ranges of values [2,3b]. Nevertheless the observed carbonyl frequencies are higher for (**2**) than for (**1**) presumably due to the greater π acceptor ability of the cage phosphite ligand compared with the TPA ligand. The mean Mo—P bond distance in (**1**) [2.489(9) Å] is longer than the mean Mo—P distance [2.428(5) Å] in (**2**) and in *fac*-Mo (CO)$_3$(P(OC$_6$H$_5$)$_3$)$_3$) (3) (2.435(8) Å) [2c]. The longer Mo—P distance in the TPA complex (1) is due to the weak π-acceptor nature of the TPA ligand compared with that of the ETPB or P(OC$_6$H$_5$)$_3$ ligands; the Mo—P bond distance in (1) is very similar to that reported in [Mo(CO)$_5$TPA] [3b] (2.48 Å). The shorter Mo—P bond length in (**2**) is consistent with the observed ^{95}Mo NMR chemical shifts (-1759 and -1805 ppm, respectively) and ^1J(Mo—P) coupling constant values (127 and 229 Hz, respectively) for (**1**) [4] and (2) [2g]; i.e. a more shielded Mo nucleus and a greater coupling constant with the cyclic phosphite complex. The ranges of P—Mo—P angles are 92.39(1)–97.88(9)° in (**1**) and 91.45(8)–94.58(9)° for (**2**). It is noteworthy that these significant distortions from the ideal 90° values occur even for these ligands having virtually the smallest known cone angles (other

Table 1. Summary of crystal data, data collection, structure solution and refinement details

	(1)	(2)
(a) Crystal data		
Formula	$C_{21}H_{36}MoN_9O_3P_3$	$C_{21}H_{33}MoO_{12}P_3$,0.90(C_7H_7)
Molar mass	651.44	748.4
Color, habit	colorless, plate	colorless, block
Crystal size, mm	0.41 × 0.41 × 0.10	0.39 × 0.25 × 0.25
Crystal system	monoclinic	triclinic
a, Å	12.713(6)	11.432(2)
b, Å	31.906(13)	12.385(2)
c, Å	14.311(7)	14.378(2)
α,	90	91.000(12)
β,	110.05(4)	107.032(13)
γ,	90	102.411(12)
V, Å^3	5453(4)	1894.0(5)
Space group	$P2_1/n$	$P\bar{1}$
Z	8	2
F(000)	2688	772
d_{calc}, g cm^{-3}	1.587	1.312
μ, mm^{-1}	0.699	0.524
(b) Data acquisition at 294K[a]		
Unit-cell reflcns (θ-range °)	25 (7.5 13.6)	25 (11.1 15.4)
Max. θ (°) for reflcns	24.9	26.9
hkl range of reflcns	−15 14; 0 37; 0 17	−14 13; 0 15; −18 18
Decay in 3 standard reflcns	15	25
Reflcns measured	9921	8200
Unique reflcns	9525	8200
R_{int}	0.035	—
Reflcns with $I > 2\sigma(I)$,	4334	3828
Absorption correction type	ψ-scans	ψ-scans
Min. max. abs. corr.	0.6570, 0.9973	0.7967, 0.8884
(c) Structure solution and refinement[b]		
Refinement on	F^2	F^2
Solution method	Patterson heavy atom	Patterson heavy atom
H-atom treatment	riding	riding
No. of variables in L.S.	403	245
Weights:		
k in $w = 1/(\sigma^2Fo^2+k)$ $[P = (Fo^2+2Fc^2)/3]$	$(0.0533P)^2$	$(0.1880P)^2$
R, R_w, GOF	0.083, 0.172, 0.94	0.098, 0.311, 0.98
Density range in final Δ-map, e Å^{-3}	−0.653, 0.900	−0.727, 1.152
Final shift/error ratio	−0.001	−0.061

[a] Data collection on an Enraf Nonius CAD4 diffractometer with graphite monochromatised Mo—Kα radiation (λ 0.71067 Å).

[b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.*, 1989, **22**, 384) for refinement with observed data on F, or with SHELXL-93 (G. M. Sheldrick, 1993) for refinement with all data on F^2.

than for PH_3). In the case of (3), the P—Mo—P angles ranged from 85.58(11) to 95.05(11)°, and other distorted angles around the Mo atom likewise reflected the larger cone angle of $P(OC_6H_5)_3$ (128°) [3d]. Consequently, steric effects are expected to have a major influence on ^{95}Mo chemical shifts, as has been verified in a separate study [2g].

CONCLUSION

These structural studies on the complexes of $[Mo(CO)_3(PTA)_3]$ and $[Mo(CO)_3(ETPB)_3]$ indicate that the Mo—P bond distances are consistent with the interpretation of the ν_{co} stretching frequencies and the ^{95}Mo chemical shift and ^1J(Mo—P) coupling con-

Table 2. Selected bond lengths (Å) and angles (°)

(1)	(2)
Mo(1)—P(11) 2.488(3)	Mol(1)—P(1) 2.434(2)
Mo(1)—P(12) 2.506(3)	Mo(1)—P(2) 2.423(2)
Mo(1)—P(13) 2.488(3)	Mo(1)—P(3) 2.426(2)
Mo(2)—P(21) 2.484(3)	
Mo(2)—P(22) 2.488(3)	
Mo(2)—P(23) 2.478(3)	
Mo(1)—C(11) 1.989(12)	Mo(1)—C(1) 1.950(10)
Mo(1)—C(12) 1.950(11)	Mo(1)—C(2) 1.982(10)
Mo(1)—C(13) 1.933(12)	Mo(1)—C(3) 2.009(9)
Mo(2)—C(21) 1.963(12)	
Mo(2)—C(22) 1.976(11)	
Mo(2)—C(23) 1.970(12)	
O(11)—C(11) 1.146(12)	O(1)—C(1) 1.166(11)
O(12)—C(12) 1.169(11)	O(2)—C(2) 1.156(10)
O(13)—C(13) 1.178(11)	O(3)—C(3) 1.136(10)
O(21)—C(21) 1.143(12)	
O(22)—C(22) 1.148(11)	
O(23)—C(23) 1.175(12)	
P(11)—Mo(1)—P(12) 92.39(10)	P(1)—Mo(1)—P(2) 91.93(7)
P(11)—Mo(1)—P(13) 96.78(10)	P(2)—Mo(1)—P(3) 94.58(9)
P(13)—Mo(1)—P(12) 97.88(9)	P(1)—Mo(1)—P(3) 91.45(8)
P(21)—Mo(2)—P(22) 93.51(10)	
P(21)—Mo(2)—P(23) 93.43(10)	
P(22)—Mo(2)—P(23) 93.16(10)	

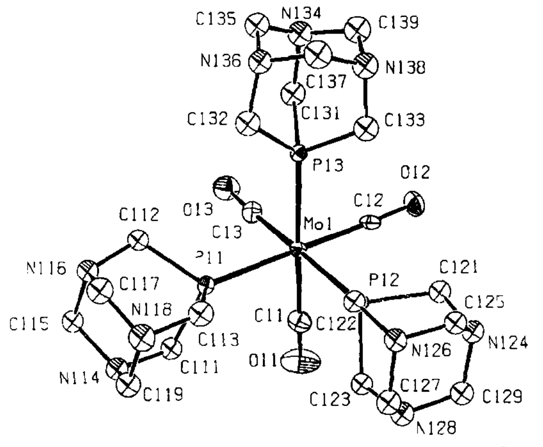

Fig. 1. A view of one of the two molecules of [Mo(CO)$_3$(TPA)$_3$] (**1**) with our numbering scheme. Probability ellipsoids are at the 30% level.

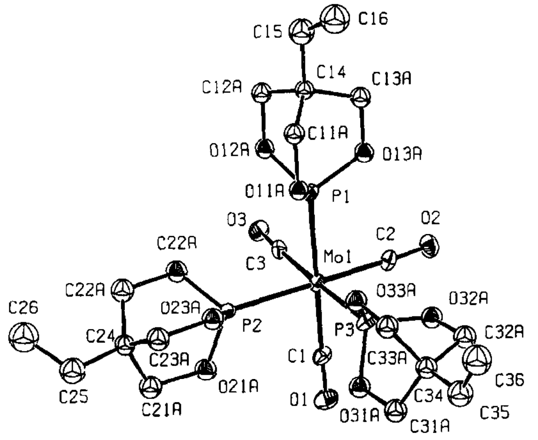

Fig. 2. A view of [Mo(CO)$_3$(ETPB)$_3$] (**2**) with our numbering scheme. Probability ellipsoids are at the 30% level.

stant data, which show that the greater π-acceptor ability of the cage phosphite ETPB ligand leads to upfield δ(^{95}Mo) and a higher *J* value. Most importantly, it is clear that significant steric effects exist in these *fac*-complexes even with the smallest known phosphine and phosphite ligands.

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