

Preliminary communication

SYNTHESIS OF *fac*-[(i-PrNH)₃P]₃Mo(CO)₃: A UNIQUE TRIS(TRIAMINO-PHOSPHINO)MOLYBDENUM TRICARBONYL

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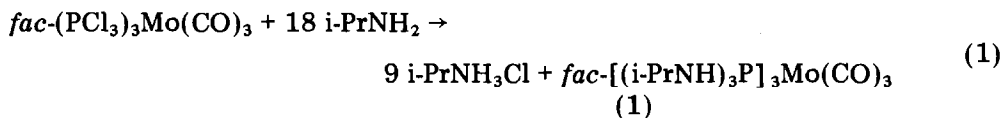
(Received December 9th, 1985)

Summary

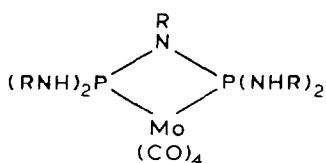
Iso-PrNH₂ reacts with *fac*-(CO)₃Mo(PCl₃)₃ to form *fac*-[(i-PrNH)₃P]₃Mo(CO)₃, a complex containing a unique combination of secondary amino-group functionality and tris(aminophosphino) substitution on molybdenum.

Although examples of tris(phosphino)molybdenum tricarbonyls, L₃Mo(CO)₃ (L = phosphine), are known [1, 2], tricarbonyls containing 3 aminophosphino moieties, i.e. (RR'N)₃P, coordinated to molybdenum are rare [3, 4]. Attempts to synthesize such molecules by (Me₂N)₃P reaction with Mo(CO)₆ or C₇H₈ · Mo(CO)₃ (C₇H₈ = cycloheptatriene) result instead in formation of the tetracarbonyl disproportionation products *cis*- and *trans*-[(Me₂N)₃P]₂Mo(CO)₄ [5, 6]. Recently we undertook studies of (CO)₃Mo(PCl₃)₃-amine reactions and found that with i-PrNH₂, the new complex *fac*-[(i-PrNH)₃P]₃Mo(CO)₃ is formed, apparently the first example of a highly functional tris(secondary aminophosphino)-substituted molybdenum tricarbonyl.

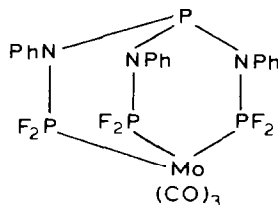
Reaction of i-PrNH₂ (75 mmol) with *fac*-(PCl₃)₃Mo(CO)₃ [7] (4.0 mmol) in toluene during 8 h at 25°C [8] results in rapid elimination of i-PrNH₃Cl and formation of *fac*-[(i-PrNH)₃P]₃Mo(CO)₃ (1) [9, 10] as shown in eq. 1.



The reaction is analogous to those between $(\text{CO})_5\text{MoPCL}_3$ and RNH_2 ($\text{R} = \text{H, Me, i-Pr, Ph, NPh}$) which yield the monophosphinoamine complexes $(\text{CO})_5\text{MoP}(\text{NHR})_3$ [11–14]. During a longer reaction period, 60 h at 25°C , i-PrNH_2 and $(\text{PCL}_3)_3\text{Mo}(\text{CO})_3$ react further to the diphosphinoamine complex $\text{i-PrN}[(\text{i-PrNH})_2\text{P}]_2\text{Mo}(\text{CO})_4$ (2) [9, 15]. In contrast, the Et_3N (24 mmol)

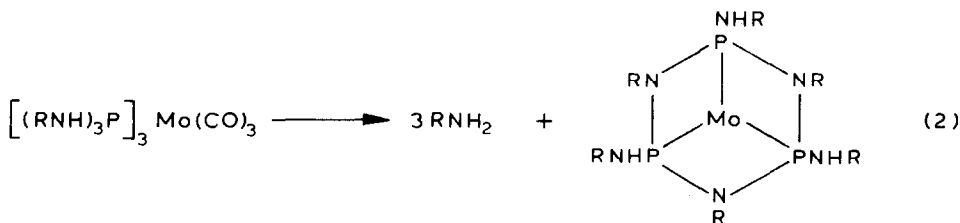


(2, R = i-Pr; 3, R = Ph)



(5)

promoted reaction of PhNH_2 (20 mmol) with $(\text{PCL}_3)_3\text{Mo}(\text{CO})_3$ (2.3 mmol) at 25°C forms directly the diphosphinoamine complex $\text{PhN}[(\text{PhNH})_2\text{P}]_2\text{Mo}(\text{CO})_4$ (3) [16, 17] without formation of an isolatable tris complex, e.g. $[(\text{PhNH})_3\text{P}]_3\text{Mo}(\text{CO})_3$. Although the tris(triaminophosphino) complex 1 forms, it does not appear inclined to undergo metal templated P–N bond condensation and cyclo-oligomerization to a facially-coordinated cyclic product (4) as in eq. 2, in a



(4)

reaction analogous to that whereby $[(\text{PhNH})_3\text{P}]_2\text{Mo}(\text{CO})_4$ eliminates PhNH_2 to form 3 [16].

Compound 1 was characterized by spectral data (MS, IR, ^1H and ^{31}P NMR) [10] and a single crystal X-ray analysis. Single crystal X-ray data were collected at $26\text{--}28^\circ\text{C}$ using a Syntex P1 automated diffractometer (Mo-K_α radiation (λ 0.71069 Å), graphite monochromator). Crystal data: $\text{MoP}_3\text{N}_9\text{O}_3\text{C}_{30}\text{H}_{72}$, formula weight 797 amu, trigonal crystal system, $R3$, $a = b = 19.906(7)$ Å, $c = 9.441(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 3241(2)$ Å³, $Z = 3$, $D_{\text{obs}} = 1.23$, $D_{\text{calc}} = 1.22$ g cm⁻³. Intensity data: $\theta\text{--}2\theta$ scan mode, $3.0^\circ < 2\theta < 35.0^\circ$, 1815 reflections measured (635 unique) of which 432 were observed [$F_0^2 > 3\sigma(F_0^2)$]. The Mo and P atoms were located by heavy-atom methods, remaining atoms were located from a three dimensional difference map. The Mo and P atoms were treated anisotropically. Data were reduced using Syntex (now Nicolet), and Northwestern University computing routines [18]. Refinement converged at $R = 0.037$ and $R_w = 0.045$.

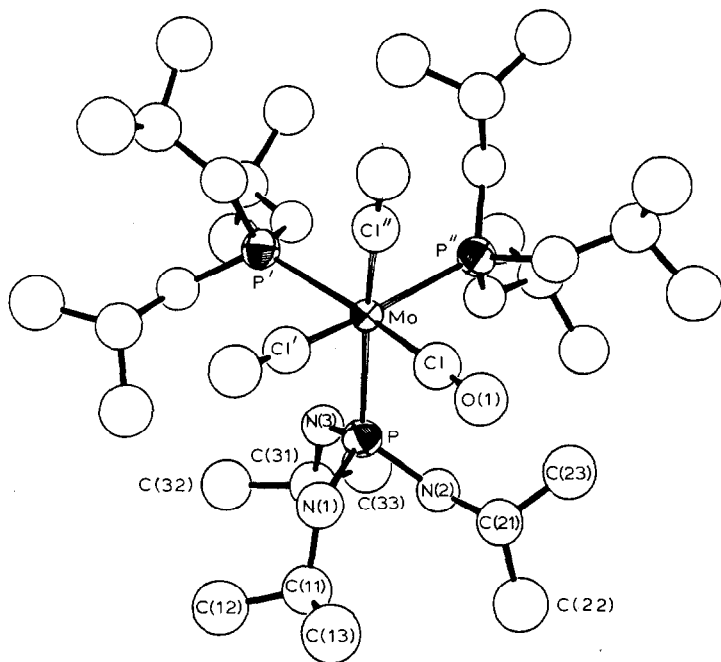


Fig. 1. Structure of *fac*-[(*i*-PrNH)₃P]₃Mo(CO)₃ (1) showing the atom numbering scheme. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms omitted for clarity.

TABLE 1

Selected Bond Distances (Å) and Bond Angles (°) in *fac*-[(*i*-PrNH)₃P]₃Mo(CO)₃ (1)

Mo—P	2.545(7)	N(1)—C(11)	1.49(2)
Mo—C(1)	1.90(2)	N(2)—C(21)	1.50(2)
P—N(1)	1.67(1)	N(3)—C(31)	1.51(2)
P—N(2)	1.67(1)	C(1)—O(1)	1.21(2)
P—N(3)	1.65(2)		
Mo—P—N(1)	106.4(5)	C(1)—Mo—C(1')	86.6(7)
Mo—P—N(2)	126.6(5)	N(1)—P—N(2)	98.7(6)
Mo—P—N(3)	112.4(4)	N(1)—P—N(3)	116.2(6)
Mo—C(1)—O(1)	179(2)	N(2)—P—N(3)	96.5(6)
P—Mo—P	93.9(2)	P—N(1)—C(11)	130(1)
P—Mo—C(1)	87.3(5)	P—N(2)—C(21)	124.8(9)
P—Mo—C(1')	92.0(6)	P—N(3)—C(31)	127.4(9)
P—Mo—C(1'')	173.8(5)		

The structure of 1 is shown in Fig. 1. Selected intramolecular bond parameters are listed in Table 1. Three (*i*-PrNH)₃P molecules are facially-coordinated to the Mo(CO)₃ unit forming a complex with crystallographic and molecular point group *C*₃ symmetry. The presence of a single sharp ³¹P NMR resonance and two characteristic carbonyl IR stretching absorptions confirms the facial isomeric structure in solution also. The conformation at each tri(amino)phosphine moiety is of the distorted *C*_s type, similar to the situation observed previously in other tri(amino)phosphinometal complexes [19]. In the limiting *C*_s conformation, the phosphorus lone pair electrons are parallel to one and perpendicular to two nitrogen lone pair electrons [20]. In 1, the torsion angles

around P—N bonds, C(21)—N(2)—P—Mo, C(11)—N(1)—P—Mo, and C(31)—N(3)—P—Mo, are 56, -175, and 178° [21], respectively. The mean P—N bond distance of 1.67(1) Å is within the 1.62–1.68 Å range of P—N bonds in other aminophosphino-Mo carbonyl complexes [2, 19] and is shorter than the distances of 1.69–1.73 Å reported for uncoordinated tri(amino)phosphines (PhNH)₃P [18], [(CH₂)₅N]₃P [(CH₂)₅N = piperidiny] [22] and (Me₂N)₃P [23]. The Mo—P distance of 2.55 Å is typical for phosphino-Mo complexes [2, 24]. However, the 1.90 Å Mo—C distance is shorter than usual (e.g. 1.97–2.05 Å) [2, 24, 25]. The *cis* ∠P—Mo—P (94°) and ∠C—Mo—C (87°) are greater than and less than 90°, respectively, perhaps the result of crowding among the facially coordinated (i-PrNH)₃P molecules. In light of this crowding it is surprising that **1** is stable since some molybdenum complexes with bulky phosphine substituents [26, 27] such as tricyclohexylphosphine will not add three phosphines but instead form five-coordinated complexes [27].

The unstable (i-PrNH)₃P and (NH₂)₃P [11, 23] are greatly stabilized by coordination to a Mo carbonyl moiety. In contrast, (PhNH)₃P appears stabilized less, since in both the PhNH₂/(CO)₃M(Ph)₃ reaction product and [P(NHPh)₃]₂Mo(CO)₄ [16], rapid PhNH₂ elimination occurs to form the diphosphinoamine complex **3** [17]. These metal-templated condensations resemble that reported for *fac*-[(PF₂)₂NPh]₃Mo(CO)₃ which eliminates PF₃ to form the novel complex P(PF₂NPh)₃PMo(CO)₃ (**5**) [4]. Why unsubstituted or alkyl-substituted aminophosphines might be stabilized to a greater degree than arylaminophosphines is unclear. Studies of this and ways to catalyze the condensation reactions of coordinated alkylaminophosphines are in progress currently.

Acknowledgement. Support by National Science Foundation grants CHE-7909497 and CHE-8312856, the University of Colorado Computing Center, and a Chinese Ministry of Defense fellowship to H.-J. C. is gratefully acknowledged.

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- 8 All operations were carried out in N₂-flushed glove bags and standard vacuum-line equipment. ¹H and ³¹P NMR spectra were obtained at 90.0 and 40.5 MHz, respectively; chemical shifts were measured relative to internal Me₄Si and external H₃PO₄. Shifts downfield from the standard are given +δ values.
- 9 Satisfactory elemental analyses for **1** and **2** were obtained.
- 10 Characterization of **1** (m.p. 133–135°C): ¹H NMR (CDCl₃), δ 3.15–3.90 ppm (m, area 9, CH), 1.10–1.55 (s, area 54, CH₃), 0.90 (br s, area 9, NH); ³¹P NMR (C₆D₆), δ 109.5 ppm (s); MS, parent at *m/e* 685; IR (Nujol), characteristic absorptions at 3410w, 3370m, 1918s, 1815vs, 1166m, 1134s, 868m, and 791 cm⁻¹.
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- 15 Characterization of **2** (m.p. 116–118°C): ^1H NMR (CDCl_3) δ 3.50 ppm (br m, area 5, CH), 1.68 (d, area 4, J 7.3 Hz, NH), 1.35 (d, area 6, J 6.9 Hz, CH_3), δ 1.20 (d of d, area 24, J 6.0 Hz, CH_3); ^{31}P NMR (C_6D_6), δ 110.7 ppm (s); MS, parent at m/e 563; IR (Nujol), characteristic absorptions at 3368m, 2013m, 1914s, 1890s, 1854s, 1395m, 1364m, 1025m, 887m, 862m, 802m, 620m, and 578m cm^{-1} .
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- 21 For a chain of atoms 1–2–3–4, the sign of the angle is positive if when looking down the 2–3 bond, a clockwise motion of 1 would superimpose it on 4.
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