Journal of Organometallic Chemistry, 364 (1989) C25–C28
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 9765PC

Preliminary communication

Triphenylphosphine oxide cocrystallization of a tris(diazaphosphole)molybdenum complex

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(Received November 28th, 1988)

Abstract

Reaction of 1,2-$(NH_2)_2C_6H_4$ with $MeP(NEt_2)_2$ yields the new 1,3,2-diazaphosphole $C_6H_4(NH)_2PMe$ (**1**). **1** with cycloheptatriene · $Mo(CO)_3$ yields *fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ (**2**), which with Ph_3PO from MeCN solution forms the cocrystallate $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot Ph_3PO \cdot MeCN$ (**3**). New compounds are characterized by spectral data; an X-ray analysis of **3** confirms its structure.

Recently it was shown that improved crystallization of hydrogen-bonding organic molecules can be achieved by their cocrystallization with triphenylphosphine oxide (Ph_3PO) [1]. This is important as new classes of organic and organometallic solids with useful electrooptic [2] and electronic [3] properties are sought. It also is a valuable technique to facilitate new-molecule X-ray single crystal structure analyses. We now demonstrate that similar crystallization enhancement can be achieved with hydrogen-bond containing organometallic complexes. We wish to report characterization of the new 1,3,2-diazaphosphole $C_6H_4(NH)_2PMe$ (**1**) by its coordination to $Mo(CO)_3$ and subsequent cocrystallization with Ph_3PO to yield the complex *fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (**3**).

Reaction of 1,2-$(NH_2)_2C_6H_4$ (9.3 mmol) with $MeP(NEt_2)_2$ (8.0 mmol) at 60°C for 4 h yields the diazaphosphole $C_6H_4(NH)_2PMe$ (**1**) [4*].

(1)

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* Reference numbers with asterisks indicate notes in the list of references.

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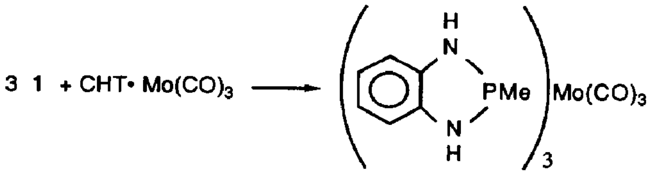
The tan oil product **1** was dissolved in toluene and filtered from excess solid 1,2-$(NH_2)_2C_6H_4$. The $^{31}P\{^1H\}$ NMR spectrum of the reaction liquid showed that it was free of unreacted $MeP(NEt_2)_2$ and contained only traces (< 5%) of uncharacterized phosphorus-containing materials. Attempts to separate **1** from these products by crystallization or chromatographic techniques were unsuccessful. Chromatography was complicated especially by the high reactivity of **1** towards moisture on plate and column solid support materials. Removal of Et_2NH and toluene from the filtrate in vacuo seemed to increase the yield of the other phosphorus-containing materials. **1** was characterized [5*] and subsequently used as obtained without removal of Et_2NH.

Three equivalents of **1** with cycloheptatriene · $Mo(CO)_3$ at 25 ° C in toluene react during 1.5 h at 25 ° C to form the complex *fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ (**2**). The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution showed mainly (> 95%) a singlet resonance at δ 133 attributable to **2**. Toluene was removed in vacuo. The resulting brown solid was slurried in 50 ml of refluxing toluene. The slurry was filtered, leaving white, solid **2** (m.p. 210 ° C, dec.). **2** is surprisingly insoluble in toluene once precipitated from it. **2** is only slightly soluble in CH_2Cl_2 or Et_2O. It is soluble in acetone, ethyl acetate and acetonitrile (hot); from the latter tiny needles could be obtained.



(2)

2

Spectral characterization data [6*] show unambiguously that **2** is a facially substituted tris(diazaphosphole)$Mo(CO)_3$ complex, since a mass spectral parent ion at *m/e* 638 $[C_{24}H_{27}P_3N_6O_3Mo^+]$ and the expected singlet ^{31}P NMR resonance and two carbonyl (CO) IR stretching absorptions are seen.

Confirmation of the structure of **2** and **1** was achieved indirectly by an X-ray single crystal analysis of **2** as the Ph_3PO cocrystallate. **2** (66 mmol) and Ph_3PO (204 mmol) were dissolved in 20 ml of acetonitrile and heated to 70 ° C. Upon cooling during 4 h, large cubic clear crystals of $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (**3**) (m.p. 192–194 ° C) precipitated from the solution [7*]. The crystals were quickly washed with petroleum ether. The crystal varied in size, but when grown slowly they could be obtained routinely as cubes in excess of 2 mm on edge. After three days at ambient temperature exposed to the atmosphere they darken, but appear to be stable indefinitely under N_2.

Compound **3** crystallizes with 2 molecules per unit cell [8*]. The structure of the complex is shown in Fig. 1. The complex consists of three Ph_3PO molecules H-bonded in nearly symmetrical fashion to a *fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ molecule. Hydrogen bonding takes place between the phosphoryl P=O units and the N–H bonds of two diazaphospholes in an approximately equilateral triangular arrangement. Complex **3** has approximate C_s symmetry in the solid; two of the diazaphosphole P–Me groups point upward and one points downward relative to the three atom P(1),P(2),P(3) plane. Bond distances within the metal complex, e.g. mean Mo–P [2.470(2) Å], Mo–C [1.992(10) Å], and C–O [1.151(13) Å], are con-

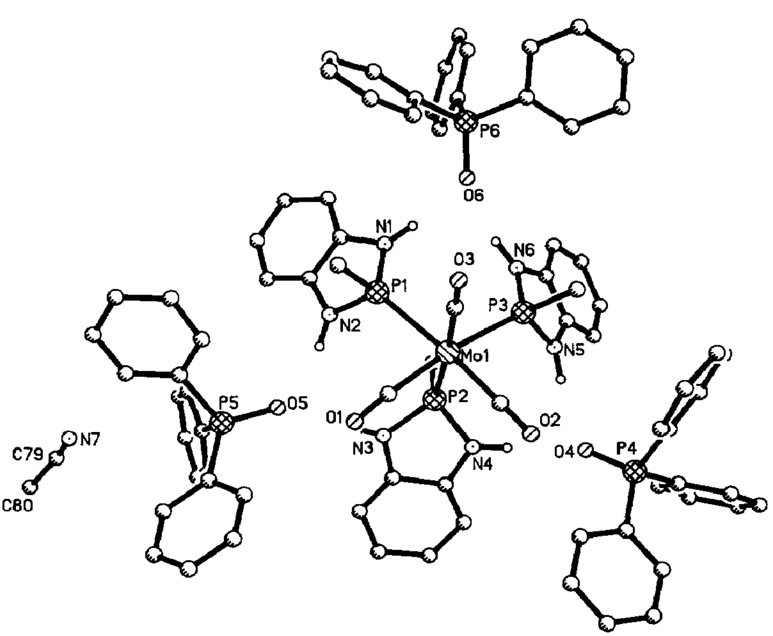


Fig. 1. Structure and atom numbering system of $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (3). Thermal ellipsoids are at the 50% level. Selected bond distances (Å) and angles (deg): mean Mo–P, 2.470(2); P–N, 1.701(8); Mo–C (CO), 1.992(10); C–O, 1.151(13); P=O, 1.494(6); C–N, 1.397(12); angles N––N, 89.3(4); Mo–C–O, 177.2(8); C–Mo–P (cis), 89.1(3); C–Mo–P (trans), 173.5(2); C–Mo–C, 89.5(4); and P(1)–Mo–P(2), 90.4(1); P(2)–Mo–P(3), 87.1(1); and P(3)–Mo–P(1), 100.2(1).

sistent with those observed previously in aminophosphine $Mo(CO)_3$ complexes [9]. Apparently the diazaphosphole units exhibit only slightly greater steric repulsion than carbonyl ligands, since the carbonyls are pushed only slightly together; the mean C–Mo–C angle is 89.5(4)°. Owing to the unsymmetrical orientation of the diazaphospholes on the $Mo(CO)_3$ moiety, the P–Mo–P angles differ somewhat. The angles P(1)–Mo–P(2), P(2)–Mo–P(3), and P(3)–Mo–P(1) are 90.4(1), 87.1(1) and 100.2(1)°, respectively. Molecular parameters for the $C_6H_4(NH)_2PMe$ diazaphosphole units, i.e. the mean P–N distance of 1.701(8) Å and the mean N–P–N internal ring angle of 89.3(4)°, are closely similar to and within the range of those reported earlier for *N*-substituted systems [10,11].

Although *N*-substituted P^{III}-1,3,2-diazaphospholes have been reported previously, unsubstituted systems have not. Our work shows that although they are oxidatively reactive, they are sufficiently stable to be used in subsequent derivatization chemistry. Their use in phosphazane oligomer/polymer synthesis and the general use of the Ph_3PO cocrystallization technique in organometallic chemistry are under further investigation.

Acknowledgements. Support of this work by National Science Foundation grant CHE-8714951, the Colorado Advanced Materials Institute, and a Dow Foundation Fellowship for E.G.B. is gratefully acknowledged.

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4 All operations were carried out under a N_2 atmosphere. ^1H and ^{31}P NMR spectra were obtained at 90.0 and 36.5 MHz, respectively. Chemical shifts were measured relative to internal Me_4Si and external H_3PO_4. Shifts downfield from the standards are given $+\delta$ values.

5 **1**: $^{31}\{^1H\}$ NMR (toluene), δ88.5 (s). ^1H NMR (toluene-d_7), δ0.7 (d, ^2J(PH) 6.5 Hz, CH_3), 4.6 (br d, NH), 6.3–7.0 (m, aryl). MS (EI$^+$), M^+, m/e 152 [$C_7H_9PN_2$], 137 [loss of CH_3].

6 **2**: Anal. Found, C, 45.96; H, 4.41, N, 12.96. $C_{25}H_{27}N_6O_3Mo$ calcd.: C, 45.30; H, 4.28; N, 13.21%. $^{31}P\{^1H\}$ NMR (acetone), δ 132.5 ppm; 132.6 ppm (CH_3CN). ^1H NMR (CD_3CN): δ 1.45 (s, CH_3), 5.25 (broad s, NH), 6.61 (s, 12H ar). MS, Cl$^-$ (NH_3 gas), M^+, m/e, 638 with the correct isotope pattern. IR (KBr): 3378.7 [(s), N–H] and 1954.1 (vs) and 1867.3 (vs) [C≡O].

7 **3**: $^{31}P\{^1H\}$ NMR (CD_3CN): δ 132.4 (s, a 1.5), 26.2 (s, a 1). ^1H NMR (CD_3CN), δ 1.45 (s, CH_3), 5.3 (broad s, NH), 6.58 (m, phenylene), 7.53–7.68 (complex m, C_6H_5). IR (KBr pellet); 3245.2 ((m, br), N–H) and 1952.2 (vs) and 1861. 5 (vs) [C≡O]. MS, (EI$^+$), M^+, m/e 638 [$(C_6H_4(NH)_2PMe)_3Mo(CO)_3$] and 277 ($Ph_3PO^+$).

8 Single crystal X-ray data for **3** were collected at 193 K using a Nicolet P3F automated diffractometer equipped with a graphite monochromator. Crystal Data: $C_{80}H_{75}N_7O_6P_6Mo$, f.w. 1512.2 amu, monoclinic, $P2_1$, a 12.869(5) b 16.312(5), c 18.853(7) Å, β 108.15(3)°, V 3761(2) Å^3, $Z = 2$. Intensity Data. ω scan mode, 5.0–45.0°, 10696 reflections measured (5119 unique) of which 4232 were observed. Data were reduced using Nicolet and SHELXTL PLUS computing routines. Refinement converged at $R = 0.046$ and $R_w = 0.053$.

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