

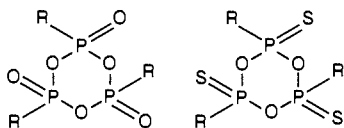
## Two Approaches to the Synthesis of Bimetallic Cage Complexes of the Tetraoxatetraphosphorinane [RPO]<sub>4</sub> Ring

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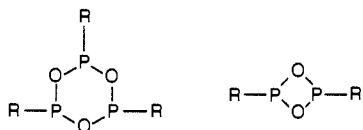
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**Abstract:** Bimetallic cage complexes of the type Mo(CO)<sub>4</sub>[RPO]<sub>4</sub>Mo(CO)<sub>4</sub> have been prepared by two synthetic routes. For R = <sup>i</sup>Pr<sub>2</sub>N and (cyclohexyl)<sub>2</sub>N, direct assemblage from Mo(CO)<sub>6</sub> and 2 equiv of the corresponding aminophosphine oxide (R<sub>2</sub>N)<sub>2</sub>P(O)H afforded Mo(CO)<sub>4</sub>[(R<sub>2</sub>N)PO]<sub>4</sub>Mo(CO)<sub>4</sub> in good yields. A single-crystal X-ray structural determination of Mo(CO)<sub>4</sub>[<sup>i</sup>Pr<sub>2</sub>NPO]<sub>4</sub>Mo(CO)<sub>4</sub> (**1**) has been completed. Crystal data [Mo Kα (λ = 0.71069)]; a = b = 13.441 (1), c = 12.469 (1) Å, Z = 2; tetragonal; space group P<sub>4</sub><sub>2</sub>/n; 3294 unique reflections, 2174 of which were considered significant; final R<sub>F</sub> = 0.044. The molecular structure features an adamantane-like cage of S<sub>4</sub> symmetry incorporating the two molybdenums with mutually orthogonal coordination spheres. Each metal is chelated by the tetraoxatetraphosphorinane [RPO]<sub>4</sub> ring, which is in a boat-boat or [2222] conformation. Significant distortion of the axial carbonyl groups is indicated by a deviation of 13° from linearity for the C-Mo-C angle. Angles around the amino nitrogens suggest multiple N-P bonding. A possible intermediate to **1** has been isolated and identified as Mo(CO)<sub>5</sub>[<sup>i</sup>Pr<sub>2</sub>NPO]<sub>3</sub>, a complex of the known heterocycle trioxatriphosphorinane [<sup>i</sup>Pr<sub>2</sub>NPO]<sub>3</sub>. This cleanly transformed to **1** at 110 °C. In a second, potentially more general approach, the phenyl-substituted analogue Mo(CO)<sub>4</sub>[PhPO]<sub>4</sub>Mo(CO)<sub>4</sub> (**5**) was assembled by nucleophilic attack of *cis*-Mo(CO)<sub>4</sub>[PhPO]<sub>2</sub><sup>4-</sup> (**4b**) on *cis*-Mo(CO)<sub>4</sub>(PhPCl<sub>2</sub>)<sub>2</sub>. The single-crystal X-ray structure of **5** confirmed its bimetallic cage structure. Crystal data: a = b = 14.9964 (7), c = 17.8053 (7) Å; Z = 4; tetragonal; space group P<sub>4</sub>/nnc; 1498 unique reflections, 1075 of which were considered significant; final R<sub>F</sub> = 0.042. Phenyl groups are twisted by 34.7° about the P-C axes, giving overall D<sub>2d</sub> molecular symmetry. Distortion of the axial C-Mo-C is minimal, and the intracage Mo-Mo separation has decreased to 4.5 from 6.1 Å in complex **1**. Chromium and tungsten analogues of **5** have also been prepared. Both **1** and **5** have enhanced stability toward nucleophilic P-O-P cleavage. Their formation, spectral, and electrochemical behavior are discussed.

Cyclic condensed metaphosphates and thiophosphates are familiar if not always well-characterized species in phosphorus(V) heterocyclic chemistry.<sup>1</sup>



By contrast, cyclic anhydrides of phosphinic acid or phosphinidene oxide [RPO]<sub>n</sub> are relatively rare. These trivalent-phosphorus heterocycles should have useful coordination chemistry as polydentate ligands leading to polycyclic and cage complexes. The first report of [RPO]<sub>3</sub> (where R = OEt, OBu, and Et<sub>2</sub>N) appeared in 1967 although full structural identification of the proposed heterocycles was not carried out.<sup>2</sup> Niecke in 1980 isolated and characterized the cyclic trimer of (diisopropylamino)phosphinic acid, [<sup>i</sup>Pr<sub>2</sub>NPO]<sub>3</sub>.<sup>3</sup> Recently, Chasaz and co-workers have synthesized and identified both [RPO]<sub>3</sub> and [RPO]<sub>2</sub> where R is the bulky 2,6-di-*tert*-butyl-4-methylphenoxy or BHT group.<sup>4</sup>



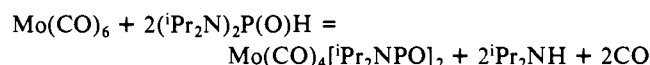
Both Niecke and Chasaz favor the intermediacy of the monomeric phosphinidene oxide (RPO). In fact, <sup>i</sup>Pr<sub>2</sub>NPO was successfully trapped as a chromium complex.<sup>5</sup>

We report here two routes to the formation of bimetallic complexes of 1,3,5,7-tetraoxa-2,4,6,8-tetraphosphorinane [RPO]<sub>4</sub> with the familiar adamantane structure common to P<sub>4</sub>O<sub>6</sub>, P<sub>4</sub>O<sub>10</sub>, and P<sub>4</sub>S<sub>10</sub>. These contain the previously unknown cyclic tetramer [RNPO]<sub>4</sub> in a boat-boat conformation serving as a tetradentate ligand chelating two metals. The geometrical constraints of the

cage structure orient the two metal coordination spheres orthogonally. In both approaches the heterocyclic ligand was assembled via coordinated phosphine precursors. A preliminary communication on **1** has appeared.<sup>6</sup>

### Results

**Direct Synthesis of 1 and 2.** The phosphine oxide (<sup>i</sup>Pr<sub>2</sub>N)<sub>2</sub>P(O)H was prepared by the hydrolysis of (<sup>i</sup>Pr<sub>2</sub>N)<sub>2</sub>PCl. Direct reaction of 2 equiv of this with Mo(CO)<sub>6</sub> in refluxing toluene for 4 h afforded complex **1** as a white solid in quantitative yields after workup. Elimination of 2 mol of <sup>i</sup>Pr<sub>2</sub>NH accompanied the complex formation.



Extension to the cyclohexyl analogue with (C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>P(O)H to give complex **2** was also successful. Use of the less sterically hindered (Et<sub>2</sub>N)<sub>2</sub>P(O)H and [(PhCH<sub>2</sub>)<sub>2</sub>N]<sub>2</sub>P(O)H, however, resulted in only trace yields of the corresponding complexes. Similarly, chromium and tungsten analogues of **1** could not be synthesized by this method.

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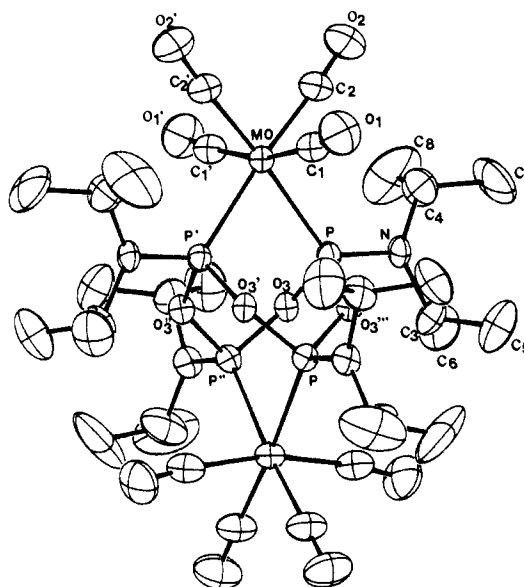
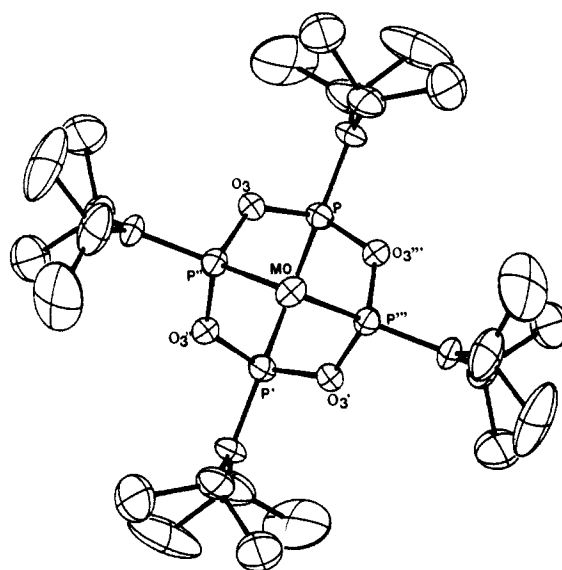
<sup>†</sup> Chemistry Division, National Research Council of Canada. NRC publication No. 29517.

Table I. Infrared and <sup>31</sup>P NMR Data

compd	IR (KBr), cm <sup>-1</sup>		<sup>31</sup> P NMR, ppm
	ν <sub>CO</sub>	ν <sub>POP</sub>	
1	2015, 1923, 1906, 1887	875	150.3
2	2015, 1922, 1905	880	148.8
3	2064, 1993, 1956, 1936, 1924	860	146.7 (A), 139.2 (M), 134.1 (X); <sup>2</sup> J <sub>AM</sub> = 10, J <sub>AX</sub> = 13, J <sub>MX</sub> = 11 Hz; <sup>3</sup> J <sub>AH</sub> = 10, J <sub>MH</sub> = 11, J <sub>XH</sub> = 9 Hz
4a	2000, 1919, 1877, 1830		144.8 (in THF)
5	2024, 1955, 1927	882	185.2
6	2014, 1970, 1930	880	211.6
7	2022, 1948, 1912	881	158.6

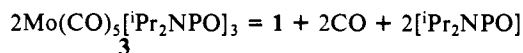
Elemental analyses of **1** were consistent with the formula Mo(CO)<sub>4</sub>[<sup>1</sup>Pr<sub>2</sub>NPO]<sub>2</sub>. Its IR spectrum exhibited typical *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> bands at 2015, 1923, 1906, and 1887 cm<sup>-1</sup>. Furthermore, a medium doublet at 875 cm<sup>-1</sup> can be assigned to POP stretching. The <sup>1</sup>H NMR spectrum consisted of a methine septet at 4.4 ppm and a methyl doublet at 1.4 ppm, assignable to the diisopropylamino group. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, a single methyl peak was observed at 24.1 ppm, along with a doublet at 47.0 ppm (<sup>2</sup>J<sub>PC</sub> = 6 Hz). Two apparent carbonyl triplets were observed at 213.0 (*J* = 15 Hz) and 207.3 ppm (*J* = 12 Hz). A <sup>31</sup>P{<sup>1</sup>H} singlet at 150.3 ppm was found. Related data of complex **2** are listed in Tables I and II. A single-crystal X-ray structural study of **1** was completed. Its molecular geometry is shown in Figure 1. This consists of an adamantane cage featuring two molybdenum tetracarbonyls chelated in a back-to-back manner by a novel tetraoxatetraphosphorinane [<sup>1</sup>Pr<sub>2</sub>NPO]<sub>4</sub> ring. The molecule has S<sub>4</sub> crystallographic symmetry and is close to 4<sub>2m</sub> symmetry. A view down the Mo–Mo axis is shown in Figure 2. Coordination around each metal is distorted from octahedral with a compressed P–Mo–P angle of 76.0 (1)°. All four carbonyls are tilted away from the cage, with *cis*-C–Mo–C angles ranging from 84.7 (2)° to 85.9 (3)°. Furthermore, the axial carbonyls are distorted from linearity with C1–Mo–C1' at only 167.3 (2)°. Metal–carbon distances are 2.039 (6) and 1.986(6) Å for carbonyls *cis* and *trans* to phosphines, respectively. Within the cage itself, the P–O–P angle is at 131.0 (2)° and P–O distances are at 1.642 (4) and 1.650 (4) Å. A listing of relevant bond distances and angles is presented in Table III.

**Isolation and Characterization of 3.** When the reaction of Mo(CO)<sub>6</sub> and (<sup>1</sup>Pr<sub>2</sub>N)<sub>2</sub>P(O)H was run at 100 °C for 4 h, <sup>31</sup>P NMR indicated presence of the unreacted phosphine oxide, **1**, as well as numerous multiplets. Workup and chromatography of the reaction mixture on neutral alumina resulted in isolation of a white solid **3**, which analyzed as Mo(CO)<sub>5</sub>[<sup>1</sup>Pr<sub>2</sub>NPO]<sub>3</sub>. It has IR carbonyl stretches at 2064, 1993, 1956, 1936, and 1924 cm<sup>-1</sup>. A POP stretch was observed at 860 cm<sup>-1</sup>. <sup>1</sup>H NMR revealed several methine septets at 3.6–3.8 ppm as well as several methyl doublets at 1.1–1.3 ppm indicative of low symmetry. The <sup>13</sup>C{<sup>1</sup>H} exhibited methine carbons at 44.0–47.4 ppm and methyls at 22.7–25.3 ppm. Carbonyl signals appeared as a doublet at 210.5 ppm (*J* = 38 Hz) and a doublet of doublets at 205.6 ppm (*J* = 4 and 16 Hz). Most informative were the <sup>31</sup>P{<sup>1</sup>H} and <sup>31</sup>P spectra, which revealed an AMX pattern centered at 146.7, 139.2, and 134.1 ppm (*J*<sub>AM</sub> = 10, *J*<sub>AX</sub> = 13, and *J*<sub>MX</sub> = 11 Hz). The

Figure 1. Molecular structure of cage complex **1**.Figure 2. View down the Mo–Mo axis of **1**. Metal carbonyls have been omitted for clarity.

proton-coupled spectrum indicated that each phosphorus is further coupled to two protons (*J* = 9–11 Hz).

Heating of complex **3** in toluene at 110 °C yielded **1** quantitatively, allowing for loss of one <sup>1</sup>Pr<sub>2</sub>NPO group per molecule of **3**.



**Assemblage of Complex 5.** The precursor of **5** was prepared by the alkaline hydrolysis of *cis*-Mo(CO)<sub>4</sub>(PhPCl<sub>2</sub>)<sub>2</sub> in aqueous

Table II. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Data

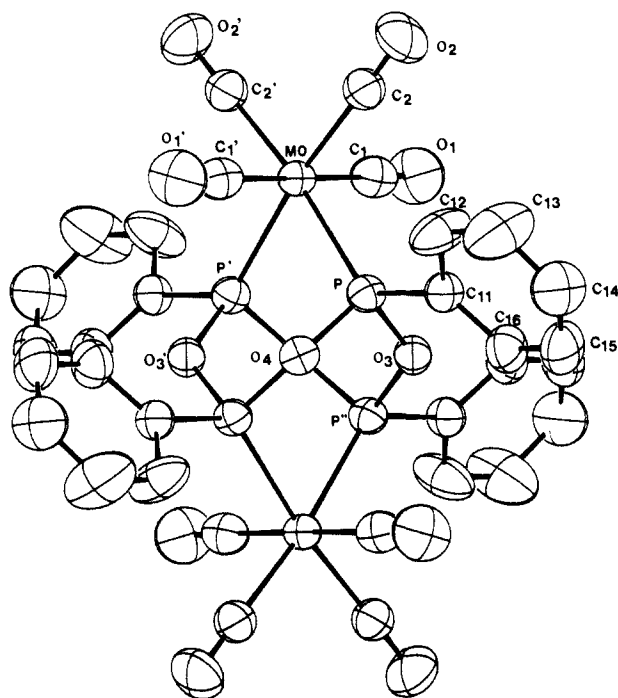
compd	<sup>1</sup> H NMR chemical shifts	<sup>13</sup> C{ <sup>1</sup> H} NMR chemical shifts <sup>a</sup>	
		alkyl and aryl	carbonyl
1	4.4 (h, 1 H); 1.4 (d, 6 H)	47.0 (d, 6 Hz); 24.1 (s)	213.0 (t, 15 Hz); 207.3 (t, 12 Hz)
2	3.9 (m, 1 H); 1.2–1.8 (m, 10 H)	56.3 (t, 6 Hz); 35.0, 26.2, 25.4	214.3 (t, 16 Hz); 207.9 (t, 13 Hz)
3	3.6–3.8 (m, 1 H); 1.1–1.3 (m, 6 H)	44.0–47.4 (m); 22.7–25.3 (m)	210.5 (d, 38 Hz); 205.6 (dd, 4, 16 Hz)
4a	7.2–7.7 (m, 10 H); 6.6 (s, 3 H); 3.2, 1.5, 0.9 (m, 36 H)	150.4 (t, 19 Hz); 129.3 (d, 7 Hz); 128.8, 127.8, 58.8, 23.9, 19.8, 13.5	220.0 (t, 7 Hz); 211.7 (t, 13 Hz)
5	7.6–7.9 (m)	143.3, 137.7, 133.5, 114.3	217.3 (t, 6 Hz); 212.0 (t, 11 Hz)
6	7.6–7.9 (m)	139.1 (t, 15 Hz); 133.2, 129.4, 128.8	223.8 (t, 16 Hz); 217.8 (t, 9 Hz)
7	7.6–7.9 (m)	138.5 (t, 29 Hz); 133.6, 129.4 (t, 10 Hz); 129.2 (t, 6 Hz)	203.9 (t, 15 Hz); 199.9 (t, 9 Hz)

<sup>a</sup>*J* values are in hertz.

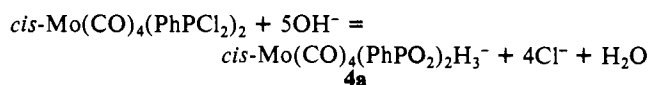
**Table III.** Selected Bond Distances (Å) and Angles (deg) for Complex 1<sup>a</sup>

Mo-P	2.5015 (15)	C1-O1	1.146 (7)
Mo-C1	2.039 (6)	C2-O2	1.154 (7)
Mo-C2	1.986 (6)	C3-C5	1.550 (9)
P-N	1.665 (4)	C3-C6	1.553 (9)
P-O3	1.650 (4)	C4-C7	1.538 (10)
P-O3'''	1.642 (4)	C4-C8	1.475 (11)
N-C3	1.506 (7)		
N-C4	1.471 (7)		
P-Mo-P'	75.96 (5)	P-O3-P''	131.0 (2)
P-Mo-C1	94.6 (2)	P-N-C4	115.2 (3)
P-Mo-C1'	95.5 (2)	P-N-C3	118.4 (4)
P-Mo-C2	99.4 (2)	C4-N-C3	125.9 (4)
P-Mo-C2'	175.2 (2)	Mo-C1-O1	172.4 (5)
C1-Mo-C1'	167.3 (2)	Mo-C2-O2	176.8 (5)
C1-Mo-C2	85.9 (3)	C5-C3-C6	110.3 (5)
C1-Mo-C2'	84.7 (3)	N-C3-C5	112.8 (5)
C2-Mo-C2'	85.3 (2)	N-C3-C6	110.8 (5)
Mo-P-O3	112.2 (1)	C7-C4-C8	112.9 (7)
O-P-O3'''	113.2 (1)	N-C4-C7	111.1 (6)
Mo-P-N	126.2 (2)	N-C4-C8	111.2 (6)
O3-P-O3'''	99.1 (2)		
O3-P-N	101.7 (2)		
O3'''-P-N	100.7 (2)		

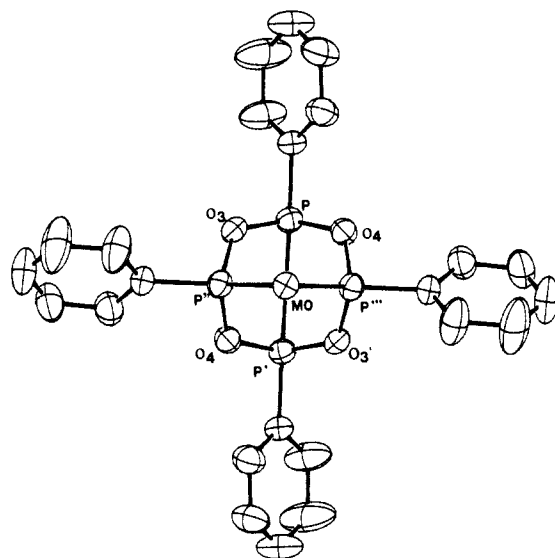
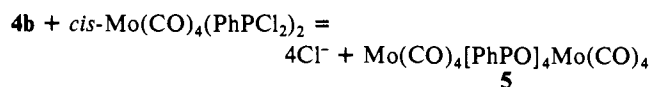
<sup>a</sup>Symmetry operations for atomic designators: one prime indicates 0.5 - x, 0.5 - y, z; two primes indicate 0.5 + y, -x, 0.5 + z; three primes indicate -y, 0.5 + x, 0.5 + z.

**Figure 3.** Molecular structure of cage complex 5.

THF and subsequent precipitation of the product **4a** at pH 7 as the tetrabutylammonium (TBA) salt.



Complex **4a** is a triprotic acid with  $pK_a$ 's of 3.5, 7.0, and 10.3. It is readily deprotonated by sodium hydride in THF to give the tetraanion  $\text{Mo}(\text{CO})_4(\text{PhPO}_2)_2^{4-}$  (**4b**). Reaction of **4b** with  $cis\text{-Mo}(\text{CO})_4(\text{PhPCl}_2)_2$  afforded up to 50% yields of  $\text{Mo}(\text{CO})_4\text{-}[\text{PhPO}]_4\text{Mo}(\text{CO})_4$  (**5**) as a white solid.

**Figure 4.** View down the Mo-Mo axis of **5**. Metal carbonyls have been omitted for clarity.**Table IV.** Selected Bond Distances (Å) and Angles for Complex 5<sup>a</sup>

Mo-P	2.4354 (19)	C1-O1	1.119 (10)
Mo-C1	2.040 (8)	C2-O2	1.135 (9)
Mo-C2	2.023 (7)	C11-C12	1.361 (11)
P-O3	1.639 (3)	C11-C16	1.374 (10)
P-O4	1.647 (3)	C12-C13	1.407 (12)
P-C11	1.801 (6)	C13-C14	1.347 (14)
		C14-C15	1.348 (14)
		C15-C16	1.387 (10)
P-Mo-P'	77.74 (6)	P-O3-P'	126.2 (3)
P-Mo-C1	94.1 (2)	P'-O4-P''	129.5 (3)
P-Mo-C1'	86.5 (2)	Mo-C1-O1	179.1 (7)
P-Mo-C2	97.3 (2)	Mo-C2-O2	176.9 (7)
P-Mo-C2'	173.2 (2)	P-C11-C12	118.3 (6)
C1-Mo-C1'	179.2 (3)	P-C11-C16	122.3 (5)
C1-Mo-C2	89.3 (3)	C12-C11-C16	119.4 (6)
C1-Mo-C2'	90.1 (3)	C11-C12-C13	118.9 (7)
C2-Mo-C2'	88.1 (3)	C12-C13-C14	121.1 (8)
Mo-P-O3	113.55 (11)	C13-C14-C15	119.9 (8)
Mo-P-O4	111.06 (9)	C14-C15-C16	120.5 (7)
Mo-P-C11	128.1 (3)		
O3-P-O4	101.8 (2)		
O3-P-C11	98.6 (3)		
O4-P-C11	100.0 (3)		

<sup>a</sup>Symmetry operations for atomic designators: one prime indicates x, 1.5 - y, 0.5 - z; two primes indicate 0.5 - x, y, 0.5 - z.

Complex **5** has carbonyl stretches at 2024, 1955, and 1927  $\text{cm}^{-1}$ . A POP stretch is observed at 882  $\text{cm}^{-1}$ . Its  $^1\text{H}$  NMR exhibited phenyl peaks at 7.6-7.9 ppm.  $^{13}\text{C}\{^1\text{H}\}$  spectrum in the carbonyl region consists of apparent triplets at 217.3 ppm ( $J = 6$  Hz) and 212.0 ppm ( $J = 11$  Hz). A single-crystal X-ray diffraction study of **5** was completed to confirm its cage structure. The molecular geometry is shown in Figure 3. A view down the metal-metal axis is presented in Figure 4. The molecule has overall  $D_{2d}$  symmetry with phenyl groups twisted by 34.7 (3) $^\circ$  from the equatorial metal coordination planes. The P-Mo-P angle is at 77.74 (6) $^\circ$  while the axial carbonyls are near linearity at 179.2 (3) $^\circ$ . The Mo-P distances are at 2.435 (2) Å, Mo-C(ax) is at 2.040 (8) Å, and Mo-C(eq) is at 2.023 (m) Å. The cage P-O-P angle is 127.8 (4) $^\circ$ . Other important bond distances and angles are listed in Table IV.

The chromium analogue of **5**, complex **6**, can be similarly assembled from  $cis\text{-Cr}(\text{CO})_4(\text{PhPO}_2)_2^{4-}$  and a mixture of  $cis$ - and  $trans\text{-Cr}(\text{CO})_4(\text{PhPCl}_2)_2$  in low yield (20%). Similarly, the tungsten analogue, **7**, was synthesized in 40% yield.

Cyclic voltammograms of **1** and **5** were run in methylene chloride. In both cases two irreversible one-electron oxidation waves were observed. For **1**, these are at 1.15 and 1.52 V (vs

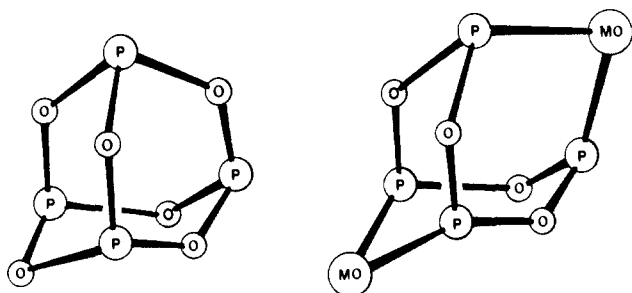
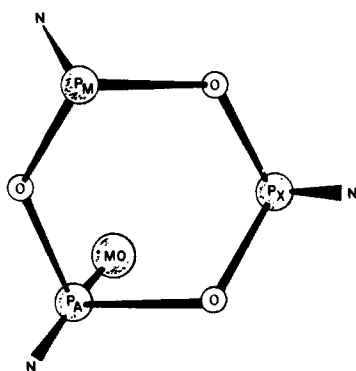
Figure 5. Relationship of P<sub>4</sub>O<sub>6</sub> to cages 1 and 5.

Figure 6. Proposed structure of complex 3.

Ag/AgCl) while values of 1.3 and 1.57 V were observed for 5.

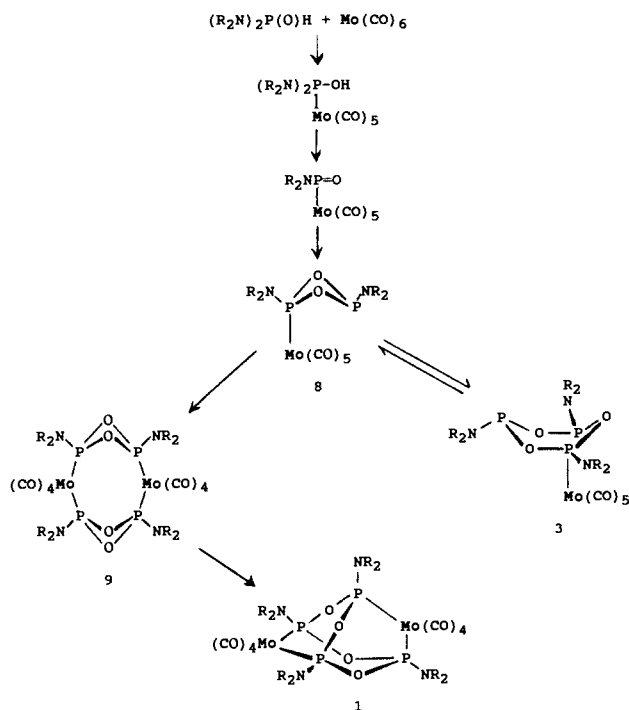
### Discussion

**Complex 1.** The cage geometry of **1** has a direct parallel in the structure of P<sub>4</sub>O<sub>6</sub> (Figure 5).<sup>7</sup> In fact, the internal P–O distances (1.64–1.65 Å compared to 1.66 Å), O–P–O (99.5° compared to 100°) and P–O–P (131° compared to 127°) angles are reasonably similar. Not surprisingly, the replacement of two bridging oxygens by two Mo(CO)<sub>4</sub> groups resulted in large cage distortions along the metal–metal axis. The Mo–Mo separation is in excess of 6.0 Å. Steric interactions of the isopropyl methine hydrogens severely distort the axial carbonyls from linearity to 167°. Lesser equatorial interactions also close up the C–Mo–C angles to about 85°. We believe that these structural constraints imposed by the rigid cage structure will have an important bearing on the chemistry of cage **1**.<sup>8</sup> Each nitrogen is essentially planar, indicative of sp<sup>2</sup> hybridization and multiple P–N bond character, consistent with the P–N distance of 1.665 (4) Å.<sup>9</sup>

**Complex 3.** The structure of **3** (Figure 6) can be assigned from its spectral data and X-ray data of [iPr<sub>2</sub>NPO]<sub>3</sub> reported by Niecke et al.<sup>3</sup> In the solid state the trioxaphosphorinane [RPO]<sub>3</sub> heterocycle is known to adopt a boat conformation for R = iPr<sub>2</sub>N and a distorted boat for R = BHT.<sup>3,4</sup> In solution both species exhibited AX<sub>2</sub> patterns in their <sup>31</sup>P NMR spectra indicative of a boat structure. For complex **3**, the AMX <sup>31</sup>P NMR spectrum can be derived from the AX<sub>2</sub> spectrum of [iPr<sub>2</sub>NPO]<sub>3</sub> (140.3 and 131.1 ppm) if one of the two high-field phosphorus is coordinated to a Mo(CO)<sub>5</sub> moiety, resulting in a complex of low symmetry. The low-field multiplet at +146.7 ppm can be assigned to this nucleus. The carbonyl <sup>13</sup>C NMR of **3** is also of interest since it suggests a hindered rotation around the Mo–P bond that resulted in two types of equatorial carbonyl signals. Unfortunately, high-temperature data could not be obtained since **3** is quantitatively converted to **1** at elevated temperatures.

**Formation of Cage 1.** While the mechanism of formation of complex **1** has yet to be delineated, it seems likely that the co-

### Scheme I



ordinated diaminophosphinous acid (iPr<sub>2</sub>N)<sub>2</sub>POH should be formed as a first step. In absence of metal carbonyl, the phosphine oxide is unchanged under these reaction conditions. One speculative mechanism is presented in Scheme I. Elimination of one of the two bulky diisopropyl amino groups at each phosphorus center serves as the driving force for P–O–P linkages. Scheme I also invokes the intermediacy of the coordinated aminophosphinidene oxide or aminophosphenite [iPr<sub>2</sub>NPO] monomer, dimer, and trimer (complex **3**). The existence of Cr(CO)<sub>5</sub>–[iPr<sub>2</sub>NPO] was convincingly demonstrated by Niecke et al.<sup>5</sup> A <sup>31</sup>P NMR spectrum of the reaction mixture after 4 h at 100 °C contained 50% phosphine oxide, 30% complex **3**, and 10% AX<sub>2</sub> as well as other small multiplets. Our successful isolation of complex **3** and its conversion to **1** lend support to this scheme. One possible precursor to **1** could be the coordinated 1,3-dioxo-2,4-diphosphetane (**8**). A related heterocycle has been reported by Chasaz.<sup>10</sup> Dimerization of this complex with CO loss would yield the valence tautomer of complex **1,9**, requiring only a skeletal rearrangement to afford **1**. Both the (Et<sub>2</sub>N)<sub>2</sub>P(O)H and [(PhCH<sub>2</sub>)<sub>2</sub>N]<sub>2</sub>P(O)H reactions led to complex multiplets in the respective <sup>31</sup>P NMR spectra. Similarly, attempts at preparing Cr and W analogues of **1** also resulted in complex NMR spectra of the reaction mixtures. In these cases, either the elimination of dialkylamine or the loss of a *cis*-CO from the metal center must be retarded, resulting in only trace yields of the symmetrical cage product. The importance of steric bulk at the carbon α to the amine nitrogen is clearly borne out by the successful synthesis of the dicyclohexylamino cage (**2**).

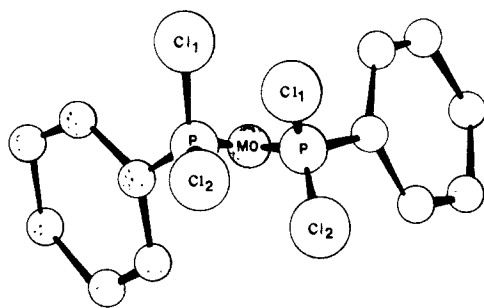
**Complex 5.** Hydrolysis of *cis*-Mo(CO)<sub>4</sub>(PhPCl<sub>2</sub>)<sub>2</sub> using aqueous THF and NaOH followed by neutralization and precipitation as the TBA salt afforded *cis*-Mo(CO)<sub>4</sub>(PhPO<sub>2</sub>)<sub>2</sub>H<sub>3</sub><sup>−</sup> (**4a**) in 90% yield. This white complex presumably has its four oxygens constrained in a square or rectangular array by the three bridging protons. <sup>1</sup>H NMR in acetone-*d*<sub>6</sub> showed a pH-dependent, broad, singlet at 6.6 ppm, which can be readily deuterated. The parent acid of this complex, *cis*-Mo(CO)<sub>4</sub>(PhPO<sub>2</sub>)<sub>2</sub>H<sub>4</sub>, has not been isolated. Acidification of aqueous solutions of **4a** precipitated a colorless oil, which rapidly decomposed to free phosphine oxide. Titration of **4a** yielded pK<sub>a</sub>'s of 3.5, 7.0, and 10.3. Deprotonation of **4a** with NaH in THF yielded a light yellow solution of *cis*-Mo(CO)<sub>4</sub>(PhPO<sub>2</sub>)<sub>2</sub><sup>4−</sup> (**4b**). Reaction of this with *cis*-Mo(CO)<sub>4</sub>-

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Figure 7. Likely conformation for *cis*-Mo(PhPCl<sub>2</sub>)<sub>2</sub>.Table V. Comparison of Structural Data for **1** and **5**

	<b>1</b>	<b>5</b>
Distances, Å		
Mo–Mo	6.001 (1)	4.531 (1)
Mo–P	2.501 (2)	2.435 (2)
Mo–C (eq)	1.986 (6)	2.023 (7)
Mo–C (ax)	2.039 (6)	2.040 (8)
P–O (av)	1.646 (4)	1.642 (4)
Angles, deg		
P–Mo–P	75.96 (5)	77.74 (6)
C–Mo–C (eq)	85.3 (2)	88.1 (3)
C–Mo–C (ax)	167.3 (2)	179.1 (7)
P–O–P (av)	131.0 (2)	127.7 (3)

(PhPCl<sub>2</sub>)<sub>2</sub> for 24 h resulted in a white precipitate, which contained NaCl and complex **5**. Formation of **5** should involve nucleophilic attack by the four phosphorus oxygens on the four coordinated P–Cl groups. The moderate yield of **5** (50%) is probably due to incomplete cage formation. CPK models of *cis*-Mo(PhPCl<sub>2</sub>)<sub>2</sub> indicate a likely orientation for the two phenyl and four chloro groups of the *cis*-phosphines as that in Figure 7. Substitution of Cl1 from one PhPCl<sub>2</sub> and Cl2 from the other by the two geminal nucleophilic oxygens of a coordinated PhPO<sub>2</sub><sup>2-</sup> will result in an incorrect orientation that cannot attain cage closure. A <sup>31</sup>P NMR of the reaction mixture revealed complex multiplets consistent with side products that had failed to complete the chloride displacements.

The even lower yield (15–20%) of complex **6**, the chromium analogue of **5**, is due to the difficulty of obtaining pure *cis*-Cr(CO)<sub>4</sub>(PhPCl<sub>2</sub>)<sub>2</sub> since the trans isomer is invariably present in equilibrium. By contrast, pure *cis*-Cr(CO)<sub>4</sub>(PhPO<sub>2</sub>)<sub>2</sub>H<sub>3</sub><sup>-</sup> was obtained, because the P–OH–O–P hydrogen bonding favors a *cis* geometry for the four P oxygens.

**[RPO]<sub>4</sub> Heterocycle.** Although the tetraoxatetraphosphorinane is still unknown in the uncomplexed state, close relatives such as [mesityl–PS]<sub>4</sub> and [MePNMe]<sub>4</sub> are well-characterized.<sup>11,12</sup> A Mo(CO)<sub>3</sub> complex has been isolated for the latter tetraphosphazane.<sup>13</sup> In all these cases, the ring adopts a crown shape unsuitable for bimetallic coordination. By contrast, our synthetic approach led to a boat–boat [2222] conformation for the resulting heterocycle.

**Comparisons of **1** and **5**.** It is instructive to compare the cage geometries of **1** and **5** (Table V). The P<sub>4</sub>O<sub>4</sub> portion of the cages are not significantly different between the two. P–O bonds are at 1.64–1.65 Å, O–P–O angles at 99–102°, and P–O–P angles at 126–131°. It is in the Mo coordination sphere, however, that the effect of a P-phenyl versus a P-N<sup>i</sup>Pr<sub>2</sub> substituent is most clearly seen. The severe distortion from idealized octahedral symmetry in **1** is not observed in **5**. Specifically, the axial C–Mo–C bending away from linearity of 13° is absent in **5**. The equatorial C–Mo–C of **1** is more compressed at 85.3° than that in **5** (88.1°). The Mo–C–O angles are bent in **1** at 172°. A longer

Mo–P distance of 2.501 Å is in **1** compared to 2.435 Å in **5**. Most revealing is the intracage Mo–Mo separation, which is decreased from over 6.0 Å in **1** to 4.53 Å in **5**. These suggest a much more congested steric environment around the metal centers in **1**; a fact reflected in its reaction chemistry to be reported in more detail later.<sup>8</sup>

Both **1** and **5** are white solids that can be stored indefinitely under nitrogen. In air, slow metal oxidation results in a blue-green coloration indicative of oxomolybdenum species. Unlike other metal-coordinated P–O–P linkages, complex **1** is not degraded by aqueous NaOH in THF or liquid ammonia. Cage **5** is slightly less stable and is slowly degraded by aqueous base to give monometallic species. Comparison of the infrared CO stretches and cyclic voltammetry data suggests that **1** has a more electron-rich metal center. This can be reconciled with lone-pair donation from the amino nitrogen into the cage phosphorus atoms.

## Conclusion

Using reactions of coordinated phosphine derivatives, we have prepared bimetallic cage complexes of the unknown tetraoxatetraphosphorinane [RPO]<sub>4</sub> by two different methods. Direct synthesis is possible with bulky bis(dialkylamino)phosphine oxides and molybdenum hexacarbonyl. The alternative and potentially more general approach used the reaction of *cis*-M(PhPCl<sub>2</sub>)<sub>2</sub> and *cis*-M(PhPO<sub>2</sub>)<sub>2</sub><sup>4-</sup> to assemble the same basic P<sub>4</sub>O<sub>6</sub> cage structure. Distortions of cage metal coordination geometry and intracage metal–metal separation are sensitive to the P substituent. The consequence of this on the reaction chemistry of these novel complexes is under investigation.

## Experimental Section

All manipulations were carried out with standard Schlenk techniques under an atmosphere of prepurified nitrogen. The solvents THF and diethyl ether were predried with calcium hydride and distilled from sodium benzophenone ketyl. Toluene was distilled from sodium. Methylene chloride and hexane were distilled from calcium hydride. Diisopropylamine was distilled from KOH. Dichlorophenylphosphine was purchased from Strem Chemicals and distilled before use. Dicyclohexylamine and phosphorus trichloride were used as purchased. Molybdenum, tungsten, and chromium hexacarbonyls were used as received from Pressure Chemicals, Inc. <sup>1</sup>H NMR spectra were recorded on Varian 360A and JEOL FX90Q spectrometers. <sup>13</sup>C and <sup>31</sup>P NMR were obtained with the JEOL FX90Q using deuterium lock. <sup>13</sup>C shifts were referenced to internal TMS while <sup>31</sup>P shifts were referenced to external 85% phosphoric acid. Infrared spectra were recorded on a Perkin-Elmer 283B instrument. Elemental analyses were performed at the University of New Hampshire Instrumentation Center with a Perkin-Elmer 240B elemental analyzer. All compounds described below gave satisfactory C, H, and N analyses.

**Bis(*N,N*-diisopropylamino)phosphine Oxide, (iPr<sub>2</sub>N)<sub>2</sub>P(O)H.** Phosphorus trichloride (59.3 g, 0.431 mol) was combined with 350 mL of methylene chloride in a 1-L three-necked flask with a mechanical stirrer and addition funnel. While the solution was cooled to –78 °C and vigorously stirred, diisopropylamine (218 g, 2.16 mol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. The white suspension was diluted with 100 mL of ether and filtered. The filtrate was evaporated to dryness under vacuum and 200 mL of hexane added to the residue. With stirring, 60 mL of diisopropylamine followed by 7.8 mL of water was added dropwise. After 1 h, the suspension was reduced in volume and filtered. The hexane filtrate was washed with water, dried over sodium sulfate, filtered, and evaporated to give a white solid, yield of phosphine oxide 61.8 g (58%). This can be recrystallized from cold hexane. IR (KBr pellet): 2334 (P–H) 1220 (P=O) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR: δ 4.4 (s). <sup>1</sup>H NMR: δ 3.55 (d, 4 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, <sup>3</sup>J<sub>PH</sub> = 17 Hz, NCHC<sub>2</sub>); 1.25 (two d, 24 H, CCH<sub>3</sub>); 7.2 (d, 1 H, <sup>1</sup>J<sub>PH</sub> = 540 Hz, PH).

**Mo(CO)<sub>6</sub>[(iPr<sub>2</sub>N)P(O)]<sub>4</sub>Mo(CO)<sub>4</sub> (**1**).** An amount of 3.0 g, 12.1 mmol, of (iPr<sub>2</sub>N)<sub>2</sub>P(O)H and 1.75 g, 6.7 mmol, of Mo(CO)<sub>6</sub> were combined with 15 mL of toluene in a 50-mL flask, and the resulting mixture was refluxed for 4 h. After removal of volatiles in vacuo, the residue was chromatographed on silica gel with 10% ethyl acetate in hexane. Evaporation of the eluant yielded a white or beige solid, which can be further purified by washing with cold acetone. Yields of 95% were typically obtained.

**Bis(*N,N*-dicyclohexylamino)phosphine Oxide, [(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>N]<sub>2</sub>P(O)H.** This was prepared from PCl<sub>3</sub> and dicyclohexylamine analogously to (iPr<sub>2</sub>N)<sub>2</sub>P(O)H. IR (KBr pellet): 2320 (P–H) 1200 (P=O) cm<sup>-1</sup>.

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Table VI. Crystallographic Data for Complexes 1 and 5

complex	1	5
formula	Mo <sub>2</sub> P <sub>4</sub> O <sub>12</sub> N <sub>4</sub> C <sub>32</sub> H <sub>56</sub>	Mo <sub>2</sub> P <sub>4</sub> O <sub>12</sub> C <sub>32</sub> H <sub>20</sub>
formula wt	1004.68	912.28
space gp	P4 <sub>2</sub> /n	P4/nnc
cryst syst	tetragonal	tetragonal
a, Å	13.441 (1)	14.9964 (7)
c, Å	12.469 (1)	17.8053 (7)
Z	2	4
d <sub>calc</sub> , g cm <sup>-3</sup>	1.481	1.51
μ, mm <sup>-1</sup>	0.738	7.25
cryst dimens, mm	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.3
radiatn, Å	Mo Kα (λ = 0.710 69)	Cu Kα <sub>1</sub> (λ = 1.540 56)
data colld	0° < 2θ < 60°	0° < 2θ < 120°
scan	θ/2θ	θ/2θ
no. of unique reflns	3294	1498
no. of obsd reflns	2174	1075
F(000)	976	1808
R <sub>F</sub>	0.044	0.042
R <sub>wF</sub>	0.054	0.049

<sup>31</sup>P{<sup>1</sup>H} NMR: δ 7.8 (s). <sup>31</sup>P NMR: (d q, <sup>1</sup>J<sub>PH</sub> = 552 Hz, <sup>3</sup>J<sub>PH</sub> = 15 Hz).

Mo(CO)<sub>4</sub>[(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>NPO]<sub>4</sub>Mo(CO)<sub>4</sub> (2). An amount of 1.80 g, 4.4 mmol, of the phosphine oxide and 0.58 g, 2.2 mmol, of Mo(CO)<sub>6</sub> were refluxed in 20 mL of toluene for 4 h. The light brown solution was evaporated down to an orange oil. This was dissolved in 5 mL of methylene chloride and deposited onto 5 g of silica gel. After vacuum evaporation, the residue was extracted twice with 20 mL of hexane. The hexane extract was concentrated and chilled to precipitate a white powder. Yields of complex 2 were 50–60%.

Mo(CO)<sub>4</sub>[Pr<sub>2</sub>NPO]<sub>3</sub> (3). An amount of 4.00 g of (Pr<sub>2</sub>N)<sub>2</sub>P(O)H and 2.40 g of Mo(CO)<sub>6</sub> were combined in 20 mL of toluene and heated in an oil bath maintained at 100 °C for 4 h. The clear yellow solution was concentrated to ca. 10 mL and filtered. A viscous oil remained after removal of volatiles. This was dissolved in 10 mL of methylene chloride and deposited onto 10 g of alumina (neutral, Brockman grade I). After evaporation, the light yellow powder was extracted with 10 mL of hexane and the extract evaporated to an oil and chromatographed on a 2 × 15 cm column of neutral alumina. Fractions were collected with hexane eluant. The first eluant fractions showing a single spot by TLC (hexane/alumina) were combined and evaporated to yield a sticky solid. <sup>31</sup>P NMR showed this to be essentially pure 3. For an analytical sample, this was redissolved in 2 mL of hexane and chilled in a dry-ice/acetone bath. The fine white precipitate was filtered cold and dried to give 160 mg of pure complex 3.

Thermolysis of 3. An amount of 50 mg of complex 3 was dissolved in 1 mL of toluene in a Schlenk tube. This was heated in an oil bath at 115 °C for 1.5 h. The product was loaded onto silica gel and chromatographed to give 35 mg of complex 1.

Mo(CO)<sub>4</sub>[PhPO<sub>2</sub>]<sub>2</sub>H<sub>3</sub> (Tetra-*n*-butylammonium salt, 4a). An amount of 1.00 g, 1.77 mmol, of *cis*-Mo(CO)<sub>4</sub>[PhPCl<sub>2</sub>]<sub>2</sub> (prepared from NBD-Mo(CO)<sub>4</sub> and PhPCl<sub>2</sub>) was dissolved in 10 mL of THF. A 20-mL solution of 0.44 M NaOH was added dropwise over 1 h with stirring. After the pH was adjusted to ca. 8, 10 mL of water was added to the reaction mixture. The THF was removed in vacuo and the resulting aqueous solution filtered. TBABr (2.26 g, 7.04 mmol) was added to the filtrate with rigorous stirring. The pH was adjusted to 7, and the white precipitate was filtered and washed with cold water and diethyl ether. Drying under vacuum afforded 1.09 g (85%) of the product.

Mo(CO)<sub>4</sub>[PhPO]<sub>4</sub>Mo(CO)<sub>4</sub> (5). Added to a 50-mL flask were 15 mL of THF, 1.29 g (1.77 mmol) of 4a, and 0.21 g (8.85 mmol) of sodium hydride (50% dispersion in oil prewashed with hexane), and the mixture was stirred until effervescence stopped. Excess NaH was filtered off with a sintered-glass frit and the filtrate stirred with 1.0 g (1.77 mmol) of *cis*-Mo(CO)<sub>4</sub>[PhPCl<sub>2</sub>]<sub>2</sub> in 10 mL of THF. After 1 day, the white precipitate was filtered off and extracted with 5 mL of methylene chloride. Filtering and addition of hexane to the filtrate precipitated out complex 5 as white crystals in up to 50% yield.

Cr(CO)<sub>4</sub>[PhPO]<sub>4</sub>Cr(CO)<sub>4</sub> (6). Complex 6 was prepared from a *cis*/trans mixture of Cr(CO)<sub>4</sub>[PhPCl<sub>2</sub>]<sub>2</sub> and Cr(CO)<sub>4</sub>[PhPO<sub>2</sub>]<sub>2</sub>H<sub>3</sub>TBA in an analogous manner to 5. Yields were usually 15–20%.

W(CO)<sub>4</sub>[PhPO]<sub>4</sub>W(CO)<sub>4</sub> (7). Complex 7 was prepared from *cis*-W(CO)<sub>4</sub>[PhPCl<sub>2</sub>]<sub>2</sub> and W(CO)<sub>4</sub>[PhPO<sub>2</sub>]<sub>2</sub>H<sub>3</sub>TBA in an analogous manner in 40% yields.

Determination of pK<sub>a</sub>'s for Complex 4a. The slope method was used to calculate the pK<sub>a</sub>'s with data from a titration of an alkaline solution of 4a with HCl.<sup>15</sup>

Table VII. Atomic Parameters x, y, z, and B<sub>eq</sub> (Esd's in Parentheses)

	x	y	z	B <sub>eq</sub> <sup>a</sup>
Mo	1/4	1/4	0.99064 (5)	2.64 (3)
P	0.21188 (10)	0.14200 (10)	0.83251 (11)	2.36 (6)
O1	0.0295 (3)	0.3270 (3)	1.0308 (4)	6.0 (3)
O2	0.2043 (4)	0.1019 (3)	1.1790 (3)	6.1 (3)
O3	0.30774 (22)	0.13153 (22)	0.7506 (3)	2.43 (13)
N	0.1702 (3)	0.0254 (3)	0.8368 (3)	2.73 (19)
C1	0.1072 (4)	0.2983 (5)	1.0088 (4)	4.0 (3)
C2	0.2194 (5)	0.1547 (5)	1.1078 (4)	4.2 (3)
C3	0.1492 (4)	-0.0212 (4)	0.7293 (5)	3.9 (3)
C4	0.1697 (5)	-0.0264 (5)	0.9407 (5)	5.6 (4)
C5	0.0376 (5)	-0.0459 (6)	0.7129 (6)	6.8 (4)
C6	0.2136 (5)	-0.1159 (5)	0.7127 (5)	6.1 (4)
C7	0.0805 (8)	-0.0976 (6)	0.9493 (7)	9.6 (6)
C8	0.2658 (8)	-0.0760 (6)	0.9610 (7)	10.8 (6)

<sup>a</sup>B<sub>eq</sub> is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table VIII. Atomic Parameters x, y, z, and B<sub>iso</sub> (Esd's in Parentheses)

	x	y	z	B <sub>iso</sub> <sup>a</sup>
Mo	0.44343 (5)	3/4	1/4	3.05 (4)
P	0.31700 (12)	0.82077 (12)	0.31177 (9)	3.12 (7)
O1	0.4455 (4)	0.5832 (4)	0.3584 (3)	6.8 (3)
O2	0.5968 (4)	0.8353 (4)	0.3479 (3)	6.5 (3)
O3	1/4	3/4	0.3534 (3)	3.3 (3)
O4	1/4	0.8677 (3)	1/4	3.1 (3)
C1	0.4444 (5)	0.6427 (5)	0.3205 (4)	4.2 (4)
C2	0.5404 (5)	0.8069 (5)	0.3128 (4)	4.0 (3)
C11	0.3186 (5)	0.9061 (4)	0.3829 (4)	3.3 (3)
C12	0.3841 (6)	0.9689 (6)	0.3799 (5)	6.3 (5)
C13	0.3843 (7)	1.0377 (7)	0.4336 (6)	8.7 (6)
C14	0.3212 (7)	1.0423 (6)	0.4873 (5)	6.4 (5)
C15	0.2566 (7)	0.9799 (6)	0.4903 (4)	5.6 (4)
C16	0.2561 (6)	0.9100 (5)	0.4393 (4)	4.6 (4)
H12	0.435	0.966	0.336	6.3
H13	0.433	1.093	0.430	8.1
H14	0.321	1.096	0.530	7.3
H15	0.202	0.983	0.533	6.5
H16	0.204	0.857	0.442	5.3
Ca1	1/4	1/4	0.318 (3)	50.3 (68)
Ca2	0.382 (3)	0.3026 (20)	0.2337 (21)	25.5 (23)

<sup>a</sup>B<sub>iso</sub> is the mean of the principal axes of the thermal ellipsoid.

X-ray Structural Determination of Complex 1. A summary of crystal data, data collection, and structure refinement is presented in Table VI. The intensities of a 0.3 × 0.3 × 0.3 mm crystal were collected with monochromated Mo Kα radiation generated at 50 kV and 16 mA with the θ/2θ scan technique and line profile analysis.<sup>16</sup> A total of 5513 measurements was made of which 3294 constitute the unique set and 2174 are considered significant at the 3σ(I<sub>net</sub>) level. The agreement between symmetry-related reflections is 0.009 (Σσ<sub>I<sub>net</sub></sub>/ΣI<sub>net</sub>) for 1521 pairs of significant reflections. Corrections were applied for Lorentz and polarization effects, but absorption corrections were not made.<sup>17</sup> Cell parameters were obtained from accurate setting angles of 44 reflections with 2θ > 50°. A Patterson map revealed the Mo atom position, which subsequently revealed the remaining atomic positions. The structure refined to R<sub>F</sub> = 0.044 and R<sub>w</sub> = 0.054. Hydrogen atoms were not located. Scattering curves were taken from the *International Tables for X-ray Crystallography*, and all computations were carried out on the NRC PDP-8e system of programs adapted for the VAX 11/780 computer.<sup>18,19</sup> Final fractional coordinates and equivalent isotropic thermal factors are listed in Table VII. Anisotropic thermal parameters and structure factor tables are included in the supplementary material.

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**X-ray Structural Determination of Complex 5.** The diffraction intensities of an approximately  $0.3 \times 0.3 \times 0.3$  mm crystal were collected with graphite monochromatized Cu K $\alpha$  radiation with the  $\theta/2\theta$  scan technique and profile analysis to  $2\theta_{\max} = 120^\circ$ .<sup>16</sup> A total of 1498 unique reflections were measured, of which 1075 were considered significant with  $I_{\text{net}} > 2.5\sigma(I_{\text{net}})$ . Lorentz and polarization factors were applied, and absorption corrections were made ( $\mu = 7.25 \text{ mm}^{-1}$ ). The minimum transmission coefficient was 0.3150 while the maximum value is 0.4316. The cell parameters were obtained by least-squares refinement of the setting angles of 50 reflections with  $2\theta > 120^\circ$  ( $\lambda(\text{Cu K}\alpha_1) = 1.54056 \text{ \AA}$ ). The structure was solved by MULTAN,<sup>19</sup> and H atom positions were calculated. The structure was refined by full-matrix least-squares methods to final residuals of  $R_F = 0.042$  and  $R_wF = 0.049$  for the significant data ( $R_F = 0.059$  and  $R_wF = 0.051$  for all data) with counting statistics weights. The final atomic positional parameters and the equivalent isotropic thermal

factors are listed in Table VIII. Other details of the refinement were as described for complex 1.

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**Supplementary Material Available:** Tables of bond angles and distances and isotropic and anisotropic thermal parameters for 1 and 5 (5 pages); tables of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

## C-H Oxidative Addition and Reductive Elimination Reactions in a Dinuclear Iridium Complex

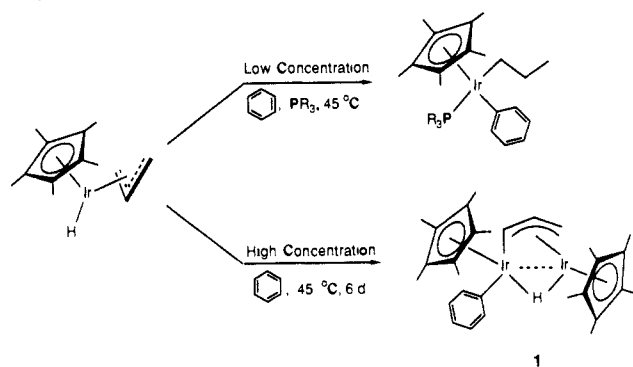
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**Abstract:** Thermolysis of the hydridoallyliridium complex  $(\eta^5\text{-C}_5\text{Me}_5)(\eta^3\text{-C}_3\text{H}_5)(\text{H})\text{Ir}$  at relatively high concentrations of starting material in benzene leads to the dinuclear benzene C-H oxidative addition product  $(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_5)\text{Ir}(\eta^1, \eta^3\text{-C}_3\text{H}_4)(\mu\text{-H})\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)$  (1). Heating this material causes reductive elimination of benzene from the dinuclear complex 1 in a clean first-order process. The lack of dependence of the rate of this process on the concentration of entering ligand demonstrates that an intermediate is formed in the reductive elimination; this species is proposed to be the coordinatively unsaturated dinuclear complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^1, \eta^3\text{-C}_3\text{H}_4)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)$  (13). Transient intermediate 13 reacts with dative ligands such as phosphines, ethylene, and *tert*-butyl isocyanide to give direct trapping products  $(\eta^5\text{-C}_5\text{Me}_5)(\text{L})\text{Ir}(\eta^1, \eta^3\text{-C}_3\text{H}_4)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)$  (2-6), formed by coordination of the ligand to one of the iridium centers. Reaction of 13 with reagents having activated X-H bonds, such as benzene-*d*<sub>6</sub>, H<sub>2</sub>, and acetonitrile, leads to intermolecular oxidative addition products having structures analogous to that of 1. Comparative inter- and intramolecular kinetic isotope effect studies have provided evidence that in the reversible reaction of 13 with benzene, an additional  $\eta^2$ -arene intermediate is not required to explain the results. Thermolysis of 2 and 4, the PMe<sub>3</sub>- and ethylene-trapped products of 13, leads to three new dinuclear complexes (7, 8, and 9). These materials are formed by intramolecular insertion into the dative ligand C-H bonds, followed by rearrangement. The structures of the intermolecular benzene C-H insertion product 1, PMe<sub>3</sub>-trapped product 2, and intramolecular C-H activation product 7 have been determined by X-ray diffraction.

There are now several examples of homogeneous intermolecular carbon-hydrogen bond activation at transition-metal centers.<sup>1</sup> In most of these cases, complexes with only one metal center are used. In the few systems reported in which more than one metal center is present in the reacting complex, little is known about the mechanism of the process in which the C-H bond is cleaved.<sup>2</sup> The reverse reaction, reductive elimination giving a newly formed C-H bond, finds ample precedent in mononuclear systems;<sup>3</sup> however, multinuclear reductive eliminations are still rare.<sup>4</sup> The two most

Scheme I



extensively studied systems are those reported by Norton and Stille. In Norton's account the intervention of a bridging metal hydride prior to reductive elimination is discussed,<sup>4b</sup> while Stille proposed a rearrangement to an intermediate that has both the alkyl and

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