2. It is apparent that the structural freedom to move the nitrogens of $\mathbf{2}^{+}\cdot$ relative to each other causes it to decompose rapidly.

We suggest that the spectral data that demonstrate flattening at nitrogen and/or through-space NN interaction in **2**, along with its facile oxidation, require that **2** exists in the inside, outside conformation **2B**. The 1-azabicyclo[6.2.2]dodecane **2** prefers i,o over o,o conformations, which models suggest have a great deal of nonbonded steric interaction between the piperidine and six-bridge methylene groups.

Acknowledgment. We thank Roger Alder (Bristol) for voluminous and fruitful correspondence, and the National Science Foundation (CHE 802611) and National Institute of Health (GM25428) for financial support of this work.

Registry No. 1, 6523-29-1; **2**, 82415-30-3; $\mathbf{2}^{2+}\cdot 2BF_4^-$, 82415-32-5; **4**, 82415-33-6; $\mathbf{5}^{2+}$, 82415-34-7; $\mathbf{6}^{2+}$, 82415-35-8; N[4.4.4]N, 71058-67-8; N[3.3.3]N, 283-58-9; 1,4-diiodobutane, 628-21-7; 9-*tert*-butyl-9-azabicyclo[3.3.1]nonane, 64776-36-9.

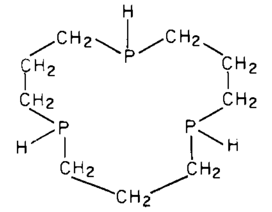
Metal-Templated Synthesis of a Macrocyclic Triphosphine–Molybdenum Complex, *fac*-$(CO)_3Mo(PHC_3H_6)_3$

Bruce N. Diel, R. Curtis Haltiwanger, and
Arlan D. Norman*

Department of Chemistry, University of Colorado
Boulder, Colorado 80309

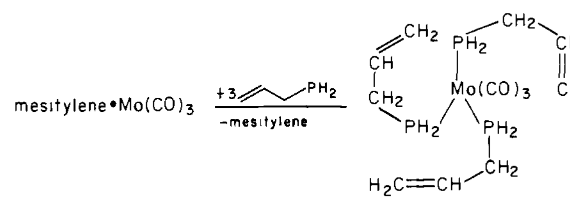
Received March 29, 1982

Numerous examples of acyclic polyphosphine ligands have been reported in recent years.[1] In contrast, many fewer examples of cyclic polyphosphines, phosphine macrocycles, have appeared.[2] The paucity of phosphine macrocycles is unfortunate in view of their potential for formation of a wide variety of novel and important transition-metal complexes. In this communication we report, from a reaction taking advantage of a kinetic template effect, the first synthesis of a metal complex containing the [12]ane-P_3 triphosphine macrocycle $(HPCH_2CH_2CH_2)_3$, **1**.[3]



1

Reaction of mesitylene·$Mo(CO)_3$ with allylphosphine[4] in benzene at 30 °C for 48 h, removal of solvent and unreacted allylphosphine in vacuo, redissolution of product in benzene, and its filtration through a 2-cm alumina column, followed by removal of solvent in vacuo, yield *fac*-$(CO)_3Mo(H_2PCH_2CH{=}CH_2)_3$ **2** (98% yield): characteristic[5,6] IR absorptions (neat, thin film or C_6H_{12} solution) 3084 (vinylic CH), 3007, 2980, 2940, 2908 (aliph CH str), 2302, 2294 (PH str), 1954, 1864 (CO str), 1633 (C=C) cm^{-1}; ^{31}P NMR (C_6D_6, rel to 85% H_3PO_4) δ 59.1 (tr, $^{1}J_{PH} = 295$ Hz, $^{1}J_{^{95}Mo-^{31}P} = 118$ Hz); ^{1}H NMR ($CDCl_3$) δ 3.92 (2, PH_2), 2.36 (2, CH_2), 5.9 (1, =CH), 5.0 (1, =CH′H, trans), 5.1 (1, =CCH′, cis); mass spectral parent ion at *m/e* 402.

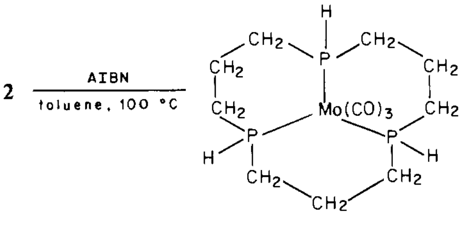


(1)

2

Characterization of **2** as a facially substituted tris(allylphosphino) complex is supported by the single ^{31}P NMR spectral resonance and the presence of two characteristic carbonyl IR absorptions.[6] That **2** is only phosphorus coordinated and not olefin coordinated is substantiated by the ^{31}P NMR coordination chemical shift, the magnitude of the $^{1}J_{PH}$ coupling constant, the presence of ^{95}Mo satellites in the ^{31}P NMR spectrum, and the lack of significant perturbation of the vinylic ^{1}H NMR or IR spectral features.

Heating of **2** in benzene 1.5 h at 75 °C with ca. 1 mol% AIBN [2,2′-azobis(isobutyronitrile)] added as free-radical initiator filtration of the solution through alumina, and removal of solvent in vacuo, followed by recrystallization from toluene, yield pure macrocyclic triphosphine complex *fac*-$(CO)_3Mo(HPC_3H_6)_3$, **3** (~85% yield).[7] ^{31}P NMR spectral analyses of reaction solutions prior to product isolation show traces of products characterized tentatively as intermediate ring cyclization products. Spectral data for **3** are as follows: characteristic[5,6] IR absorptions (cyclohexane)2330 (P–H), 1945, 1844 (CO) cm^{-1}; ^{31}P NMR (C_6D_6, rel to 85% H_3PO_4) δ 32.0 ($^{1}J_{PH} = 318$ Hz, $^{1}J_{^{95}Mo-^{31}P} = 118.4$ Hz); ^{1}H NMR ($CDCl_3$) two complex multiplets collapse on ^{31}P decoupling to δ 4.9 (area 1) and a broad complex multiplet (area 6) at δ 1.8. Homonuclear irradiation of the area-1 multiplet yield sharpened lines for the P–H resonance allowing its unambiguous assignment. The mass spectrum exhibits a parent ion at *m/e* 402 (assigned to $^{96}Mo^{12}C_{12}P_3{}^{16}O_3H_{21}{}^{+}$). Crystalline **3** undergoes only slight decomposition after several hours exposure to air or ambient moisture; however, **3** decomposes rapidly in O_2-containing solutions to as yet uncharacterized materials.



3

The macrocycle complex crystallizes from toluene in two distinct crystal habits, very thin plates[8] and needles.[9] Samples of each

---

(1) (a) Uriarte, R.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79–85. (b) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183–94. (c) Ghilardi, C. A.; Midolini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1980**, *19*, 301. (d) Christol, H.; Cristau, H. J.; Fallouk, F.; Hullot, P.; *Tetrahedron Lett.* **1979**, *28*, 2591–2594. (e) King, R. B. *Acc. Chem. Res.* **1972**, *5*, 177–188. (f) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490–1493.

(2) (a) Fox, M. A.; Campbell, K. A.; Kyba, E. P. *Inorg. Chem.* **1981**, *20*, 4163–4165. (b) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139–147. (c) Davis, R. E.; Hudson, C. W.; Kyba, E. P. *Ibid.* **1978**, *100*, 3642–3643. (d) DelDonno, T. A.; Rosen, W. *Inorg. Chem.* **1978**, *17*, 3814–3816. (e) Kyba, E. P.; Hudson, C. W.; McPhaul, N. J.; John, A. N. *J. Am. Chem. Soc.* **1977**, *99*, 8053–8054. (f) DelDonno, T. A.; Rosen, R. *Ibid.* **1977**, *99*, 8051–8052. (g) Horner, L.; King, H.; Walch, P. *Phosphorus* **1975**, *6*, 63–64.

(3) Presented in parts at the Fourth Symposium on Macrocyclic Compounds, August 11–13, 1980, Provo, UT, and the Joint Biennial Inorganic Chemistry Symposium (GWC),[2] June 5–7, 1980, Guelph, Ontario, Canada.

(4) Shay, R. H.; Diel, B. N.; Norman, A. D., submitted for publication.

(5) Thomas, L. C. "Interpretation of the Infrared Spectra of Organophosphorus Compounds"; Heyden and Sons: London, 1974.

(6) Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977. Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432–4437.

(7) All new compounds have acceptable analytical data.

(8) Crystal data for $(CO)_3Mo(PHC_3H_6)_3$ (thin plates): $a = 13.14\ (2)$ A°, $b = 9.05\ (1)$ A°, $c = 13.79\ (3)$ A°, $\beta = 92.4\ (1)°$, $V = 1638\ (5)$ Å^3. The thin plates were twinned; both fragments were indexed and gave the cell dimensions given above; the crystal was of insufficient quality for single-crystal X-ray diffraction analysis. The space group was not determined.

0002-7863/82/1504-4700$01.25/0

J. Am. Chem. Soc. 1982, 104, 4701-4703

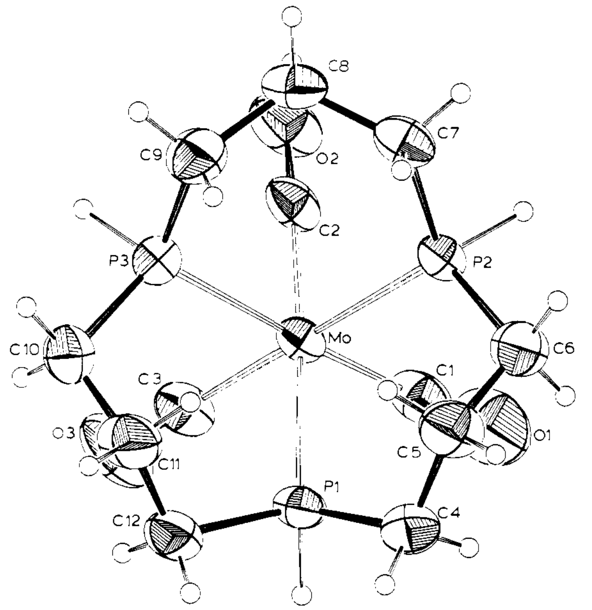


Figure 1. Molecular structure of *fac*-$(CO_3Mo(PHC_3H_6)_3$ (**3**). Selected bond lengths (Å) and angles (deg): Mo–P(1), 2.507 (1); Mo–P(2), 2.455 (1); Mo–P(3), 2.465 (1); Mo–C(1), 1.983 (4); Mo–C(2), 1.987(3); Mo–C(3), 1.962(3); C(1)–O(1), 1.142 (5); C(2)–O(2), 1.162 (4); C(3)–O(3), 1.146(4); P–C range, 1.826 (4)–1.848 (4); C–C range, 1.510 (5)–1.525 (5), ∠P–Mo–P range, 88.18 (3)–89.27 (3); ∠C–Mo–P(cis) range, 87.7 (1)–92.8 (1); ∠C–Mo–C range, 90.45 (1)–93.5 (1).

gave identical ^{31}P NMR and mass spectra. Recrystallization of **3** from CD_2Cl_2 yields only needles.[9] Single-crystal X-ray analysis of these needles results in the structure[10] shown in Figure 1. The complex consists of a [12]ane-P_3 ring, *facially* coordinated to the $Mo(CO)_3$ moiety. The molecule has approximate C_s symmetry, with a mirror plane passing through Mo, P(1), O(2), C(2), and C(8). The macrocycle ring structure is such that two of the six-membered metallocycle rings, [MoP(1)C(4)C(5)C(6)P(2) and MoP(3)C(10)C(11)C(12)P(1)], are in chair conformations while the third ring, [MoP(2)C(7)C(8)C(9)P(3)], is in a boat conformation. In contrast, in solution at 25 °C, a structure having either an all-boat or all-chain conformation or an "averaged" conformation arises, since only one ^{31}P NMR resonance is observed.

Selected bond distances and angles are given in the figure legend. The Mo–P and M–C_{CO} distances are typical of those observed in other phosphine–molybdenum(0) carbonyl complexes.[11] The principal structural distortion involves the Mo–P(1) and Mo–C(2) distances, which are slightly longer than the other Mo–P and Mo–C distances, respectively. It is noted these bonds are from Mo to the atoms that share octahedral faces with the phosphorus atoms [P(2) and P(3)] of the boat-conformation metallocycle.

The formation of the triligated *sec*-phosphine macrocyclic ligand in **3** involves anti-Markovnikov P–H bond addition across the carbon–carbon double bonds of neighboring allyl groups, in a novel metal-templated process. The reaction exemplifies the kinetic template effect since uncoordinated allylphosphine when treated with AIBN yields entirely different products.[12] The reaction is clean, resulting in only slight molybdenum carbonyl complex degradation and no evidence for intramolecular ring closure to form coordinated phosphabutane rings or intermolecular P–H bond addition. The reaction is highly regiospecific; no Markovnikov addition product has been detected.

Studies of the generality of this metal-templated cyclization approach, derivatization of the hydridomacrocycles complexes, and displacement of the macrocyclic phosphine from the metal are in progress currently.

Acknowledgment. Financial assistance through grants from the National Science Foundation (CHE 79-09497), the Colorado Energy Research Institute, the Department of Energy/Solar Energy Research Institute (DE-FG02-80CS83112), and the University of Colorado Computing Center are gratefully acknowledged.

Registry No. 2, 82456-41-5; **3**, 82456-42-6; *fac*-$(CO)_3$Mo mesitylene, 12089-15-5; AIBN, 78-67-1.

Supplementary Material Available: Tables of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

---

(9) Crystal data for $(CO)_3Mo(PHC_3H_6)_3$ (needles from CD_2Cl_2): space group $P2_1/c$, $a = 12.606$ (3) A°, $b = 8.508$ (2) A°, $c = 15.420$ (2) A°, $\beta = 93.39$ (2)°, $V = 1652.5$ (6) Å^3, $D_o = 1.61$ g cm^{-3}, $D_c = 1.616$ g cm^{-3}, $Z = 4$. Data were collected on a Syntex $P\bar{1}$ autodifractometer using graphite-monochromatized Mo Kα radiation.

(10) The structure was solved by heavy-atom techniques and refined by full-matrix least-squares calculations to $R = 0.026$ and $R_w = 0.032$ for 2685 unique observed reflections. Hydrogen atoms were located, and their positions were refined; anisotropic thermal parameters were used for the non-hydrogen atoms. Details of the refinement and structure will be published later.

(11) Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: Amsterdam, 1974.

(12) Diel, B. N.; Norman, A. D., submitted for publication.

Cleavage of the Triple Bond in Phenylacetylene by Monomeric Ru(II) and Os(II) Complexes. Formation of Stable Ru(II) Alkyls from Terminal Alkynes

B. Patrick Sullivan,*[1a] Robert S. Smythe,[1b]
Edward M. Kober,[1a] and Thomas J. Meyer*[1a]

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received November 19, 1981

Complexes of ruthenium(II) containing "classical" ligands such as ammonia, pyridine, or polypyridine, or halide ions are known to bind with either alkenes or alkynes to form stable, isolable products such as $[Ru^{II}(NH_3)_5(3\text{-hexyne})]^{2+}$.[2,3] We have extended this work to the synthesis and characterization of 2,2′-bipyridine (bpy) and 2,2′,2″-terpyridine (trpy) complexes of both Os(II) and Ru(II) with unsaturated carbon ligands. Not surprisingly, quite stable complexes can be prepared containing internal alkynes, an examle of which is shown in eq 1.[4] Quite remarkably, under the

$$cis\text{-}Os(bpy)_2Cl_2 + CH_3O_2CC{\equiv}CCO_2CH_3 \xrightarrow[\Delta]{EtOH/H_2O} cis\text{-}[Os^{II}(bpy)_2(CH_3O_2CC{\equiv}CCO_2CH_3)Cl]^+ + Cl^- \quad (1)$$

same reaction conditions but with phenylacetylene as the alkyne the carbonyl complex, *cis*-$[Os(bpy)_2(CO)Cl]^+$, is obtained.[5] The reaction is general for octahedral complexes of Ru(II) and Os(II) with one labile halide ligand in that the precursor complexes *cis*-$Ru^{II}(bpy)_2Cl_2$, *cis*-$[Ru^{II}(trpy)(bpy)Cl](PF_6)$, and *cis*-$Os^{II}$(phen)[1,2 bis(diphenylphosphino)benzene]Cl_2 (phen = 1,10-phenanthroline) all give the corresponding monocarbonyl products in 70–91% yield.[6] A somewhat related but less well-defined process has been observed as a competing reaction in the chlororuthenium(III)-catalyzed hydration of acetylenes.[7]

---

[1] (a) The University of North Carolina. (b) On leave from James Cook University, Townsville, Australia.

(2) Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368.

(3) Lehmann, H.; Schenck, K. J.; Chapuis, G.; Ludi, A. *J. Am. Chem. Soc.* **1979**, *101*, 6197. In a more general sense see: Taube, H. *Surv. Prog. Chem.* **1973**, *6*, 1.

(4) Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Organometallics*, in press.

(5) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J., to be submitted for publication.

(6) All of the carbonyl complexes were characterized by cyclic voltammetry, elemental analysis, infrared spectroscopy, and in some cases by ^1H NMR spectroscopy.

0002-7863/82/1504-4701$01.25/0