cytochrome P-450.[21] The transfer of a carbene ligand from iron to pyrrole nitrogen may offer a pathway for the destruction of cytochrome P-450 which produces green porphyrins with similar features of N-alkylated porphyrins.[22] Shifts of an oxene unit from metal to nitrogen by reaction 1 followed by further migration analogous to the N-alkylporphyrin–homoporphyrin conversion[8] could also be involved in heme oxygenase activity.[23]

(21) Mansuy, D.; Battioni, J.-P.; Chottard, J.-C.; Ullrich, V. *J. Am. Chem. Soc.* **1979**, *101*, 3971–3973 and references therein.
(22) Ortiz de Montellano, P. R.; Kunze, K. L.; Mico, B. A. *Mol. Pharmacol.* **1980**, *18*, 602–605.
(23) Joshida, T.; Kikuchi, G. *J. Biol. Chem.* **1978**, *253*, 4230–4236.

Synthesis and Molecular Structure of an Aminophosphoranide Transition-Metal Adduct. First Transition-Metal Derivative Having a Cyclic N–P–M Arrangement

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A novel structural arrangement has been found in compounds **1**, which exhibit two remarkable features: (1) the metal atom is bound to a pentacoordinated phosphorus atom, which thus acts as a *phosphoranide* ligand **2**, and (2) the metal is further bound to a nitrogen atom to form a hitherto unknown N–P–M cycle, which is all the more surprising in view of the low basicity expected from a P-bound nitrogen atom. Also very unusual is the location of the oxygen atoms in equatorial sites and of the phenyl group in an apical site of the bipyramidal phosphorus atom.

The aminophosphoranidemolybdenum adduct **1a** was obtained by allowing 1 molar equiv of LiMe to react with the cationic adduct **3a**[1] in a THF/ether solution (3:1) at −20 °C. Infrared


1a M = Mo

1b M = W
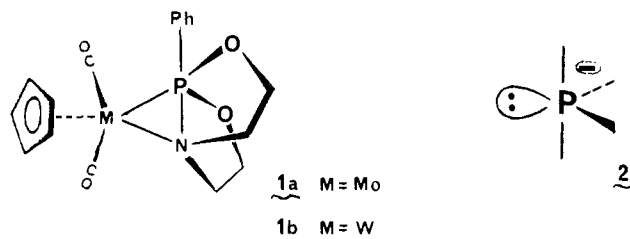
monitoring of the reaction showed that the ν(CO) vibrations of **3a** at 1850 and 1978 cm⁻¹ had completely disappeared after 30 min, while two new absorptions had developed at 1855 and 1945 cm⁻¹. The evolution of methane was ascertained by IR spectroscopy. The insoluble LiBPh₄ salt, precipitated, was filtered off, and **1** was isolated in 66% yield as yellow crystals, moderately air-sensitive, soluble in THF, CHCl₃, acetone, ether, and benzene. It is indefinitely stable at room temperature and melts (with decomposition) at ∼145 °C.

Compound **1** exhibits a single resonance in the proton decoupled ³¹P NMR spectrum at 43.9 ppm, which is an unusual location

(1) Wachter, J.; Jeanneaux, F.; Riess, J. G. *Inorg. Chem.* **1980**, *19*, 2169.
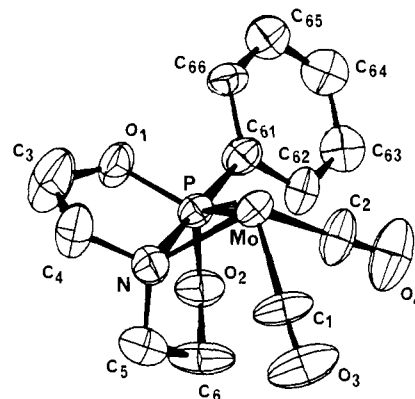
Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)(CO)_2Mo[PhP(OCH_2CH_2)_2N]$. The η^5-C₅H₅ ring has been omitted for clarity. Selected bond lengths (average): P–Mo 2.382 (4), P–N 1.908 (12), P–O₁ 1.625 (10), P–O₂ 1.624 (10), P–C₆₁ 1.856 (12), N–Mo 2.227 (10). Angles: Mo–P–N 61.7 (3), Mo–P–O₁ 119.4 (4), Mo–P–O₂ 118.4 (4), O₁–P–O₂ 115.8 (5), C₆₁–P–N 176.4 (5), O₁–P–C₆₁ 92.1 (5), O₂–P–C₆₁ 93.4 (5), Mo–N–P 69.7 (4), P–Mo–N 48.7 (3).

when compared to the 185–200-ppm range found for Mo–P^III adducts of type **3** or **4**.[1] The ¹H spectrum shows a single sharp

4
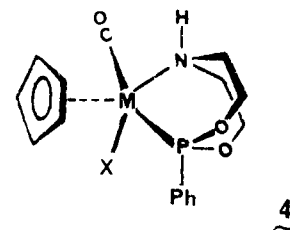
signal for the C₅H₅ protons at 5.32 ppm in CDCl₃. The ν(N–H) vibration at 3205 cm⁻¹ in **3** has disappeared.

The structure of **1** was established by X-ray diffraction. It forms triclinic crystals [space group $P\bar{1}$ with unit cell parameters a = 11.156 (1) b = 11.593 (3) c = 14.554 (1) Å; α = 101.55 (1), β = 111.35 (1), γ = 90.52 (2)°; v = 1710.53 Å³ Z = 4]. The triclinical system was determined and confirmed by Weissenberg films and powder diffraction spectra. The centrosymmetrical $P\bar{1}$ space group was established by statistical tests. The Patterson function showed the presence of four Mo atoms in the unit cell; all the nonhydrogen atoms were located by Fourier difference maps and showed the presence of two types of molecules of slightly different conformation. From 6760 measured reflections (2 < θ < 25°; Mo Kα radiation, Ge monochromator) 4681 were used for the preliminary refinement of the structure (R value = 8%).

The most prominent features (Figure 1) of the molecule are the five-connected character of the phosphorus atom, i.e., the presence of the original phosphoranide ligand; the shortest Mo^II–P bond found so far (average 2.38 Å), 0.07–0.14 Å shorter than those found in complexes having the CpMo^IIPR₃ pattern (R = OCH₃, C₆H₅);[2] the presence of the new N–P–Mo cycle (average Mo–N 2.23 Å); one of the longest P–N bonds known (average 1.91 Å);[3] an almost perfect bipyramidal arrangement of the substituents on phosphorus, with the two Mo–P–O and one O–P–O angles all close to 120° and the NPC(phenyl) atoms almost aligned (average 176°) perpendicular to the equatorial plane formed by the other substituents of P.

While phosphoranides were postulated as reaction intermediates by Wittig as early as 1967,[4] it was only in 1978 that direct evidence was provided by Granoth and Martin for the existence of an ionic lithium phosphoranide.[5] Still more recently, the first transi-

(2) Reisner, M. G.; Bernal, I.; Brunner, H.; Doppelberger, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1664.
(3) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 701. Grec, D.; Hubert-Pfalzgraf, L. G.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1980**, *102*, 7133.
(4) Wittig, G.; Maercker, A. *J. Organomet. Chem.* **1967**, *8*, 91. See also: Hellwinkel, D. *Chem. Ber.* **1969**, *102*, 528.

tion-metal phosphoranide adduct was obtained in this laboratory.[6]

Where the coordination of the nitrogen is concerned, there is as far as we know only one report of a transition-metal adduct in which the metal is linked to a P-bound *tri*connected nitrogen atom (exocyclic to a phosphazene ring)[7] and none in which the metal bridges in the P–N bond as in **1**. Only *di*connected nitrogen atoms, such as the skeletal nitrogen atoms of phosphazene rings, are expected and were shown to have a high enough basicity to easily give transition-metal adducts.[7,8]

Reaction 1 can be reversed under the action of an acid: bub-

(1)
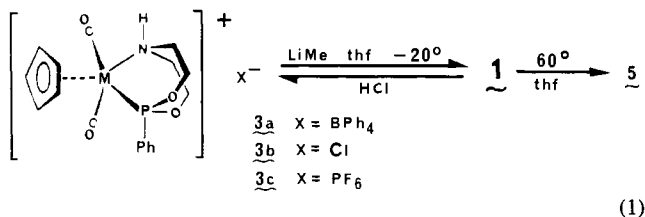
bling HCl into a THF solution of **1a** at room temperature converts it quantitatively to **3b**.[1] Upon heating for 4 h in THF at 60 °C, adduct **1a** converts to the deep red compound **5**, which was formerly synthesized by allowing LiMe to react with the hexafluorophosphate salt **3c**.[6]

5
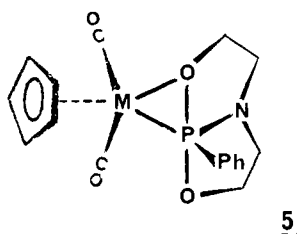
Similar behavior was observed with the tungsten analogue of **3a**, yielding the orange-yellow crystalline compound **1b** (^{31}P NMR δ 26.4, J_{P-W} = 232 Hz) whose spectral and analytical data are consistent with the same formulation.

These results confirm the exceptional versatility of the cyclic P–N ligand **6**, which had already been found to coordinate

6
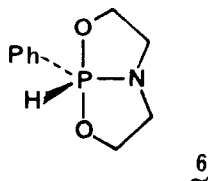
transition metals through phosphorus alone, both phosphorus and nitrogen in its tautomeric open form,[1,9] or phosphorus and oxygen (after abstraction of a proton) in its closed bicyclic form,[6] and now has been found to do so through phosphorus and nitrogen in its closed form, while under similar experimental conditions the iron analogue of **3** led to a new reaction in which the phenyl group migrates from phosphorus to the metal.[10]

Supplementary Material Available: A table of atomic positions and thermal parameters and a table of bond lengths and angles (2 pages). Ordering information is given on any current masthead page.

(5) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7434; **1979**, *101*, 4623.

(6) Wachter, J.; Mentzen, B. F.; Riess, J. G. *Angew. Chem.* **1981**, *93*, 299.

(7) Calhoun, A. P.; Paddock, N. L.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1973**, 2708.

(8) See, for example: O'Brien, J. P.; Allen, R. W.; Allcock, H. R. *Inorg. Chem.* **1979**, *18*, 2230.

(9) Pradat, C.; Riess, J. G.; Bondoux, D.; Mentzen, B. F.; Tkatchenko, I.; Houalla, D. *J. Am. Chem. Soc.* **1979**, *101*, 2234.

(10) Vierling, P.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1981**, *103*, 2466.

Organometallic Photochemistry at the Solid/Gas Interface. Photochemistry of Surface-Confined Cobalt Tetracarbonyl Monitored by Fourier Transform Infrared Photoacoustic Spectroscopy
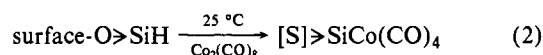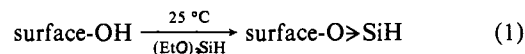
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Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139

We wish to report the photochemistry of surface-confined –Co(CO)$_4$ fragments exposed to reactive gases. Such photochemistry is of importance in establishing primary events following excitation of the molecular entity attached to the surface and is of relevance to the photoactivation of surface-confined catalysts.[1,2] We apply, for the first time, the technique of Fourier transform infrared photoacoustic spectroscopy (FTIR/PAS)[3] to monitor the photoreactions of a species on the surface including in situ monitoring of reactions involving a gas-phase species. Without any sample manipulation or preparation, this technique has allowed characterization of the photochemistry of surface species with the molecular level specificity generally possible when infrared absorption spectroscopy is used to monitor reactions of metal carbonyls in homogeneous solution. The results herein establish FTIR/PAS as a technique of unequalled capability in monitoring such surface chemistry.[4]

The system studied is [S]≫SiCo(CO)$_4$ where [S] represents a high-surface-area silica (~400 m^2/g from Alfa). The synthetic procedure follows from known reaction chemistry and was carried out according to the representation in (1) and (2).[5] The func-

$$\text{surface-OH} \xrightarrow[\text{(EtO)}_3\text{SiH}]{25\ ^\circ\text{C}} \text{surface-O}{\gg}\text{SiH} \qquad (1)$$

$$\text{surface-O}{\gg}\text{SiH} \xrightarrow[\text{Co}_2\text{(CO)}_8]{25\ ^\circ\text{C}} \text{[S]}{\gg}\text{SiCo(CO)}_4 \qquad (2)$$

tionalization of metal oxides such as SiO$_2$ using (RO)$_3$SiR' reagents[6] and reaction of Co$_2$(CO)$_8$ with R$_3$SiH to give

(1) (a) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3385. (b) Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.*, submitted for publication.

(2) (a) Scanner, R. D.; Austin, R. G.; Wrighton, M. S.; Honnick, W. D.; Pittman, C. U., Jr. *Adv. Chem. Ser.* **1978**, *No. 184*, 13. *Inorg. Chem.* **1979**, *18*, 928. (b) Hucul, D. A.; Arnold, T.; Brenner, A. "Abstracts of Papers"; 179th National Meeting of the American Chemical Society, Houston, TX, 1980; American Chemical Society: Washington, DC, 1980; INOR 7.

(3) (a) Rockley, M. G. *Chem. Phys. Lett.* **1979**, *68*, 455; **1980**, *75*, 370. *Appl. Spectrosc.* **1980**, *34*, 405, 407. (b) Rockley, M. G.; Davis, D. M.; Richardson, H. H. *Science (Washington D.C.)* **1980**, *210*, 918. (c) Vidrine, D. W. *Appl. Spectrosc.* **1980**, *34*, 314. (d) Royce, B. S. H.; Enus, J.; Teng, Y. C. *Bull. Am. Phys. Soc.* **1980**, *25*, 408. (e) Laufer, G.; Juneke, J. T.; Royce, B. S. H.; Teng, Y. C. *Appl. Phys. Lett.* **1980**, *37*, 517. (f) Royce, B. S. H.; Teng, Y. C.; Enus, J. *IEEE Symp. Ultrasonics* **1980**, *2*, 652.

(4) There are a number of techniques useful for obtaining vibrational spectra of surface species. See: Bell, A. T.; Hair, M. L. *ACS Symp. Ser.* **1980**, *No. 137*. The FTIR/PAS would appear to offer advantages when monitoring both surface and gas-phase reaction products in situ.

(5) In a typical procedure, ~1 g of high-surface-area SiO$_2$ having some –OH available is suspended in ~25 mL of alkane solvent containing excess (EtO)$_3$SiH at 25 °C under N$_2$. The solution is stirred for 24 h and then filtered to collect a solid. After repeated washing the solid exhibits an infrared signal at ~2250 cm^{-1} associated with Si–H. Infrared transmission experiments indicate that there is ~6.1 mol % of ≫SiH.[1b] The powder is then reacted with excess Co$_2$(CO)$_8$ in alkane solution under N$_2$ at 25 °C for 24 h. After repeated washing, the solid still exhibits an infrared peak at ~2250 cm^{-1} (~3.4 mol % of SiH) and signals at 2110, 2050, and ~2020 cm^{-1} characteristic of ≫SiCo(CO)$_4$ (~1.9 mol %).[1b] Reaction of the powder with Co$_2$(CO)$_8$ also leads to some decomposition of the Co$_2$(CO)$_8$ to leave a cobalt oxide/hydroxide on the surface.[1b] Samples were exposed to vacuum for 20 min at 25 °C prior to any experimentation to remove any O$_2$ or H$_2$O from the surface.

(6) (a) Arkles, B. CHEMTECH **1977**, *7*, 766. (b) Whitehurst, D. D. *Ibid.* **1980**, *10*, 44. (c) Karger, B. L.; Giese, R. W. *Anal. Chem.* **1978**, *50*, 1048A. (d) Grushka, E.; Kikta, E. J. *Ibid.* **1977**, *49*, 1004A. (e) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135.

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