$$\textit{trans,mer}\text{-}\mathrm{Ta(C_2H_4)(PMe_3)_2Cl_3}^{17} \xrightarrow[\mathrm{N_2,\ Na/Hg,\ 2\ h}]{\mathrm{PMe_3,\ ether/THF}} \underset{\mathbf{3}^{18}}{{}^1/_2\mathrm{[Cl(PMe_3)_3(C_2H_4)Ta{=}N\text{-}]_2}} \quad (4)$$

Extensive ^{1}H, ^{13}C, and ^{31}P NMR studies suggest that the two ends of this molecule are "locked" ~90° to one another when the phosphine on each Ta which is trans to the μ-N_2 ligand stops exchanging rapidly on the NMR time scale (cf. **1b**). Thirdly, **2b** and **3** react with acetone to give dimethylketazine quantitatively (eq 5). This reaction is analogous to the reaction of Ta-

$$\mathbf{2b}\text{ or }\mathbf{3} \xrightarrow[\mathrm{8\ h,\ 25\ ^\circ C}]{\mathrm{excess\ Me_2C{=}O}} \mathrm{Me_2C{=}N{-}N{=}CMe_2} \quad (5)$$

$\mathrm{(NPh)(PEt_3)_2Cl_3}$ with the carbonyl function to give an imine.[7] To our knowledge, this reaction of bridging dinitrogen is unique.

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(18) Ether-soluble yellow-orange powder, 60% yield; $\nu_{\mathrm{Ta_2N_2}}$ = 825 cm^{-1} (cf. **1a**, **2b**).

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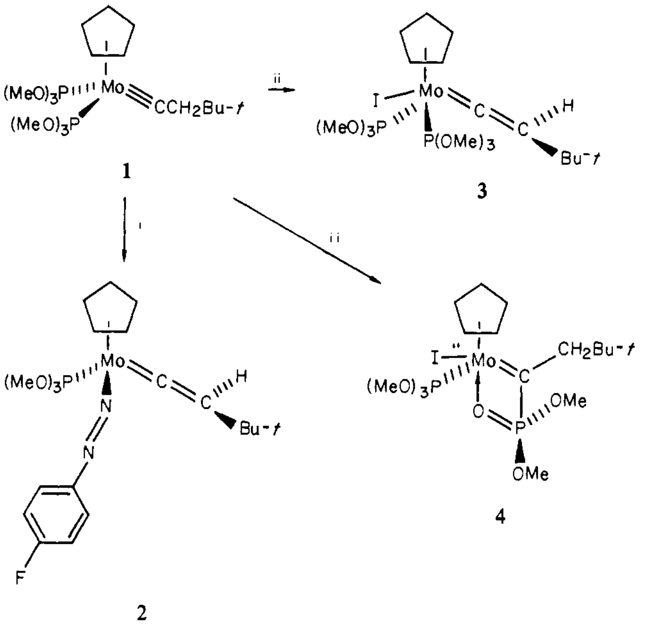
Transformation of a Molybdenum-Alkylidyne Complex into Molecules Containing Vinylalkylidene and Alkylidene Ligands. Crystal and Molecular Structure of $[\overline{\mathrm{IMo{=}C(CH_2Bu\text{-}}t\mathrm{)P(O)}}\mathrm{(OMe)_2(P(OMe)_3)(\eta^5\text{-}C_5H_5)]}$

Sir:

Alkylidene transition-metal complexes in which the carbon atom bonded directly to the metal carries either a partial negative[1] or positive charge[2] have been described. This distinction has been emphasized by the use of the descriptive terms—Schrock or Fischer-type complexes. Group 6 alkylidene chemistry has, so far, been largely dominated by Fischer-type complexes despite the obvious importance of expanding the range of alkylidene complexes in this area of the periodic table. The availability of the alkylidyne complex **1**[3] $\mathrm{[Mo{\equiv}CCH_2Bu\text{-}}t\mathrm{(P(OMe)_3)_2(\eta^5\text{-}C_5H_5)]}$, whose synthesis we have previously described, suggested a possible new synthetic approach to species containing carbon to molybdenum double bonds.

Reaction of **1** with 4-fluorophenyldiazonium tetrafluoroborate in methylene chloride at room temperature led to the rapid formation of a deep red solution. Chromatography of the reaction mixture on an alumina packed column afforded (31% yield) from hexane (−78 °C) dark red crystals, which were characterized by elemental analysis and mass, IR, and NMR spectroscopy[4] as the vinylalkylidene complex **2**. (See Scheme I.) Thus, an apparent *two*-electron oxidative reaction has occurred between an aryldiazonium salt[5] and an alkylidyne complex with loss of a molecule of trimethyl phosphite. It is likely that the displaced phosphite facilitates loss of HBF_4 from an intermediate cationic species to give the neutral vinylalkylidene complex **2**, containing a chiral molybdenum center.

Scheme I[a]



[a] (i) $\mathrm{4\text{-}FC_6H_4N_2BF_4/CH_2Cl_2}$, (ii) $\mathrm{CF_3I/Et_2O}$.

A vinylalkylidene complex was also obtained as one of the products on treatment of complex **1** with trifluoroiodomethane in diethyl ether at room temperature. Column chromatography on alumina at low temperature (−30 °C) led, on elution with hexane, to the separation of the red crystalline (−20 °C, hexane) product **3**, which was identified[6] as a molybdenum vinylalkylidene with the illustrated structure. Recent calculations[7,8] suggest that in **3** the plane of the CHBu-*t* fragment should bisect the molecular symmetry plane as shown, although the barrier to rotation is calculated to be relatively low. This prediction was borne out by the observation of *one* ^{31}P resonance at −90 °C for the two phosphite ligands present in **3**.

The formation of **3** probably involves an initial oxidative reaction followed by elimination of a proton, this being supported by the

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(1) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98-104.

(2) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59-81. Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545-574. Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487-613.

(3) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795-5796.

(4) The spectroscopic data for complex **2** is as follows: γ(Nujol) 1608 m (Mo=C=C), 1594 m ($\mathrm{MoN_2C_6H_4F}$) cm^{-1}; ^{1}H NMR ($C_6D_5CD_3$, room temperature) τ 2.49 (m, 2 H, FC_6H_4), 3.08 (t, 2 H, FC_6H_4, J_{HH} = 8 Hz), 4.15 (d, 1 H, C=C*H*Bu-*t*, J_{PH} = 6 Hz), 4.61 (s, 5 H, C_5H_5), 6.64 (d, 9 H, POMe, J_{PH} = 12 Hz), 8.78 (s, 9 H, Bu-*t*); ^{13}C NMR ($C_6D_5CD_3$, room temperature, ^{1}H decoupled) δ 31.2 (s, C*Me*$_3$), 34.7 (s, *C*Me$_3$), 52.0 (s, POMe), 96.7 (d, C_5H_5, J_{CP} = 22 Hz), 115.5 (d, FC_6H_4, J_{CF} = 25 Hz), 120.5 (d, FC_6H_4, J_{CF} = 7 Hz), 141.3 (s, C=*C*HBu-*t*), 146.4 (s, FC_6H_4), 159.4 (d, F*C*$_6$H$_4$, J_{CF} = 242 Hz), 348.6 (d, Mo=*C*=CHBu-*t*, J_{CP} = 30 Hz); ^{31}P NMR ($C_6D_5CD_3$, room temperature, ^{1}H decoupled) δ 184.7 (s).

(5) Oxidative-addition reactions between low-valent metal complexes and aryldiazonium salts have been previously observed; see: Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443-470.

(6) The spectroscopic data for complex **3** is as follows: γ(Nujol) 1605 m (Mo=C=C) cm^{-1}; ^{1}H NMR (C_6D_6, room temperature) τ 4.69 (t, 1 H, C=C*H*Bu-*t*, J_{PH} = 13 Hz), 5.08 (t, 5 H, C_5H_5, J_{PH} = 2 Hz), 6.32 (t, 18 H, POMe, J_{PH} = 5 Hz), 8.94 (s, 9 H, Bu-*t*); ^{13}C NMR (C_6D_6, room temperature, ^{1}H decoupled) δ 31.3 (t, C*Me*$_3$, J_{CP} = 3 Hz), 35.0 (t, *C*Me$_3$, J_{CP} = 6 Hz), 54.5 (t, POMe, J_{CP} = 3 Hz), 91.0 (t, *C*$_5$H$_5$, J_{CP} = 20 Hz), 132.7 (t, C=*C*HBu-*t*, J_{CP} = 12 Hz), 326.4 (t, Mo=*C*=CHBu-*t*, J_{CP} = 51 Hz); ^{31}P NMR (C_6D_6, room temperature, H decoupled) δ 157.9 (s); ^{31}P NMR ($C_6D_5CD_3$, −90 °C, ^{1}H decoupled) δ 159.3 (s).

(7) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585-590.

(8) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592-598.

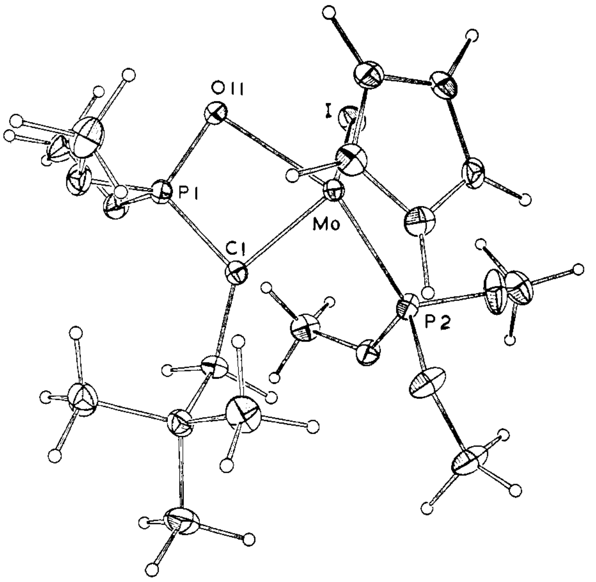

Figure 1. Molecular structure of 4 with thermal ellipsoids constructed at the 30% probability level (except for H atoms). Bond lengths: Mo–I = 2.8225 (4), Mo–P2 = 2.4309 (12), Mo–C1 = 2.006 (4), Mo–O11 = 2.226 (3), Mo···P1 = 2.7234 (12), C1–P1 = 1.743 (4), P1–O11 = 1.512 (3) Å. Bond angles: O11–Mo–C1 = 73.4 (1)°, Mo–C1–P1 = 92.9 (2)°, C1–P1–O11 = 102.1 (2)°, P1–O11–Mo = 91.5 (1)°.

presence (GC–MS) of CHF_3 in the volatile reaction products.

The synthesis of **2** and **3** from an alkylidyne represents a new approach to vinylalkylidene complexes whose chemistry is beginning to receive attention.[9–13] Previously molecules of this type have been obtained from reactions with acetylenes, and **2** and **3** represent the first examples of molybdenum complexes containing this ligand.

Elution with diethyl ether afforded the second product of the reaction between **1** and CF_3I, a green crystalline compound (**4**) (35% yield). The analytical and NMR data[14] did not unambiguously define the structure of this molecule, and therefore an X-ray diffraction study[15] was undertaken.

The molecular structure (Figure 1) illustrates that **4** is a molybdenum alkylidene complex containing a four-membered chelate ring $\overline{\mathrm{Mo{=}C1{-}P1{=}O11}}$. Molecular dimensions within this system may be compared to those of the Mn—C—P=O fragment in the compound $[(NC)_2C{=}CP(O)(OPr\text{-}i)_2Mn(CO)_2(diphos)]$.[18] Both rings are planar ($\sum$valence angles = 359.9 and 359.8°, respectively), with individual ring angles differing little between the two structures (maximum difference < 2°). Metal to ligand distances are naturally longer in the molybdenum system, but in the case of carbon this increase is somewhat offset by the alkylidene of the Mo=C1 link (Δ_{M-O} = 0.069 Å, Δ_{M-C} = 0.049 Å). The η^5-C_5H_5 ligand is oriented such that it is bisected by a plane constructed through Mo and P1 perpendicular to the chelate plane,[19] and the iodine and phosphite functions lie on the opposite side of the four-atom ring. The phosphite is cis to the alkylidene group, providing a steric rationale to the fact that the Bu-*t* group is found above (if I and P2 are below) the metallacyclic plane.

The formation of **4** is particularly interesting and represents an unusual transformation of an alkylidyne into an alkylidene complex. The reaction involves an apparent Arbuzov reaction followed by migration of the phosphonate group from the molybdenum to the alkylidyne carbon.

The chemistry and mechanism of formation of these molecules, which contain molybdenum carbon double bonds, are being investigated further.

Acknowledgment. We thank the S.R.C. for support.

Supplementary Material Available: Atomic positional and thermal parameters for alkylidene complex (4 pages). Ordering information is given on any current masthead page.

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(9) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405.

(10) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765.

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(12) Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7232–7238.

(13) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483–3486.

(14) Spectroscopic data for complex **4**: ^{1}H NMR (C_6D_6, room temperature) τ 5.12 (d, 5 H, C_5H_5, J_{PH} = 3 Hz), 6.32 (d, 3 H, P{O}OMe, J_{PH} = 10 Hz), 6.35 (d, 9 H, POMe, J_{PH} = 10 Hz), 6.60 (d, 3 H, P{O}OMe, J_{PH} = 10 Hz), 7.34 (ddd, 2 H, C*H*$_2$Bu-*t*, J_{HH} = 14, J_{PH} = 10, J_{PH} = 6 Hz), 9.04 (s, 9 H, Bu-*t*); ^{13}C NMR (C_6D_6, room temperature) δ 30.7 (s, C*Me*$_3$), 35.0 (s, *C*Me$_3$), 51.2 (d, P(O)OMe, J_{CP} = 9 Hz), 54.8 (d, POMe, J_{CP} = 8 Hz), 57.9 (dd, *C*H$_2$Bu-*t*, $^2J_{CP}$ = 9, $^3J_{CP}$ = 9 Hz), 94.5 (s, C_5H_5); ^{31}P NMR (C_6D_6, room temperature) δ 53.1 (d, P(O)OMe, J_{PP} = 27 Hz), 176.4 (d, $P(OMe)_3$, J_{PP} = 24 Hz). The ^{13}C resonance due to the carbon Mo=C was not detected.

(15) Crystallographic data for complex **4**: Crystal data: $C_{16}H_{31}IMoO_6P_2$, M = 606.2, triclinic, a = 10.3130 (16), b = 12.9811 (3), c = 9.1912 (18) Å, α = 91.751 (17)°, β = 106.166 (15)°, γ = 94.981 (16)°, V = 1175.4 (4) Å^3, ρ_{obsd} = 1.71, Z = 2, ρ_{calcd} = 1.713 g cm^{-3}, $\mu_{(Mo\ K\bar{\alpha})}$ = 18.9 cm^{-1}, $F(000)$ = 600 electrons, space group $P\bar{1}$ from E statistics and successful refinement. Of 5445 independent reflections measured on a Syntex $P2_1$ automated diffractometer (graphite monochromated Mo K$\bar{\alpha}$ radiation and the θ–2θ scan mode to a maximum 2θ of 55°), 4419 had $I > 2.5\ \sigma(I)$ and were used to solve (direct methods) and refine (full-matrix least-squares) the structure to R = 0.037, P_w = 0.042, using the SHELX 76 programs.[16] All non-H atoms have been allowed anisotropic thermal motion, while all H atoms are set in idealized positions (at C–H = 1.08 Å) with U_H = 0.06 Å^2 (C_5H_5 and CH_2) or U_H = 0.10 Å^2 (CH_3).[17]

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(17) Complete crystallographic details will be published elsewhere. One referee has correctly pointed out that following Churchill, M. R. (*Inorg. Chem.* **1973**, *12*, 1213–1214), a more realistic representation of the electron density distribution would be given by a somewhat shorter C–H distance; however, a deficiency of the SHELX 76 system is that calculated hydrogen atoms are invariably set at C–H = 1.08 Å.

(18) Newton, G. M.; Pantaleo, N. S.; King, R. B.; Diefenbach, S. P. *J. Chem. Soc., Chem. Commun.* **1979**, 55–56.

(19) In $C_5H_5ML_2$ (alkylidene) complexes in which the alkylidene function is not constrained with a ring system, the complementary relative orientation of alkylidene and cyclopentadienyl fragments is found[20] and has recently been shown[10,11] to represent the minimum energy conformation of a relatively shallow potential well upon rotation.

(20) (a) Redhouse, A. D. *J. Organomet. Chem.* **1975**, *99*, C29–C30. (b) Hädicke, E.; Hoppe, W. *Acta Crystallogr., Sect. B* **1971**, *27*, 760–768.

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Crystal Structure of a Tetranuclear Copper(II)-Inosine Monophosphate-*o*-Phenanthroline Complex: First Unambiguous Example of O_6 Coordination in a Metal-6-Oxopurine Complex

Sir:

The disputed existence of an N_7–O_6 chelate from guanine to platinum has been the subject of a lively controversy among researchers studying the mechanism of action of antitumor platinum drugs.[1,2] Although some investigators feel that there

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(1) (a) B. Rosenberg, *J. Clin. Hematol. Oncol.*, **7**, 817 (1977); (b) D. M. L. Goodgame, I. Jeeves, F. L. Phillips, and A. C. Shapski, *Biochim. Biophys. Acta*, **378**, 153 (1975); (c) M. M. Millard, J. P. Macquet, and T. Theophanides, *ibid.*, **402**, 166 (1975); (d) J. Dehand and J. Jordanov, *J. Chem. Soc., Chem. Commun.*, 598 (1976); (e) J. P. Macquet and T. Theophanides, *Bioinorg. Chem.*, **5**, 59 (1975); (f) G. Pneumatikakis, N. Hadjiliadis, and T. Theophanides, *Inorg. Chim. Acta*, **22**, L1 (1977); (g) *Inorg. Chem.*, **17**, 915 (1978).