$^2J(^{119}Sn\text{–}C\text{–}H)$ = 80.0 Hz, SnMe), 1.97–2.70 (m, 4 H, $SnCH_2CH_2$), 2.73–3.20 (m, 2 H, Sn $CH_2CH_2CH_2$), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{10}H_{14}Br_2OSSn$: C, 26.07; H, 3.06; M_r, 460.5. Found: C, 26.02; H, 3.18; M_r, 466.

3-(Dimethyl((trifluoromethyl)sulfonyl)stannyl)propyl Phenyl Sulfoxide (18). Into a three-necked 50-mL flask fitted with a dry ice–acetone cold finger was placed 1.133 g (2.862 mmol) of 3-(bromodimethylstannyl)propyl phenyl sulfoxide. The reaction flask was cooled to −78 °C, and about 35 mL of sulfur dioxide was condensed. To the clear solution was added 0.7335 g (2.862 mmol) of silver trifluoromethanesulfonate, the cooling bath was removed, and the mixture was stirred at the SO_2 reflux temperature for 1 h. The solution was then suction filtered under nitrogen, and the clear colorless filtrate was transferred to a 50-mL flask. The sulfur dioxide gas was allowed to evaporate, and the residual volatiles were removed by stirring at 58 °C (oil bath) under 0.05 torr for 3.5 h to give 1.01 g (75%) of 18 as a clear colorless gum: ^{1}H-NMR ($CDCl_3$) δ 0.76 (s, 6, $^2J(^{119}Sn\text{–}C\text{–}H)$ = 68.0 Hz, $Sn(CH_3)_3$), 1.63 (m, 2, $Sn(CH_3)_3CH_2$), 2.37 (m, 2, $Sn(CH_3)_3CH_2CH_2$), 3.04 (ddd, J_{gem} = 14.3 Hz, J_{AX} = 9.7 Hz, J_{AY} = 1.9 Hz, *H*CHSOPh), 3.36 (ddd, J_{gem} = 14.1 Hz, J_{AX} = 2.2 Hz, HC*H*SOPh), 7.67 (br s, 5, SO*Ph*); IR (KBr plate) 965 cm^{-1} (strong, S═O). Anal. Calcd for $C_{12}F_3H_{17}O_4S_2Sn$: C, 30.99; H, 3.69. Found: C, 30.91; H, 3.49.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation through Grant CHE-8318205 for support of this research. We also acknowledge assistance from the Foundation through Grant CHE-8313711 toward purchase of the 300-MHz NMR spectrometer used in this study. Chi Vu provided valuable technical assistance for which we are grateful.

Registry No. 1, 104336-11-0; 2, 29394-87-4; 3, 104336-12-1; 4, 104336-13-2; 5, 104336-14-3; 6, 104336-15-4; 7, 104336-16-5; 8, 104336-17-6; 9, 104336-18-7; 10, 104336-19-8; 11, 104336-20-1; 12, 104336-21-2; 13, 104336-22-3; 14, 104336-23-4; 15, 104336-24-5; 16, 104336-25-6; 17, 104336-26-7; 18, 104336-27-8; 19, 68725-14-4; 20, 1461-22-9; allyl alcohol, 107-18-6; 3-(trimethylstannyl)propyl tosylate, 31059-14-0; 3-(trimethylstannyl)propyl phenyl sulfide, 35935-24-1; 3-(trimethylstannyl)propyl ethyl sulfone, 104373-39-9; dichloromethylstannane, 753-73-1; tetrachlorostannane, 7646-78-8.

Communications

Reaction of (Pentamethylcyclopentadienyl)(*tert*-butylimino)phosphane with Tris(acetonitrile)tricarbonylmolybdenum(0): Evidence for a Metalloiminophosphane Intermediate

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Received May 13, 1986

Summary: $(\eta^1\text{-}Me_5C_5)P{=}N(t\text{-}Bu)$ (1) was prepared in a two-step synthesis from $Me_5C_5PCl_2$. Reaction of 1 with $(MeCN)_3Mo(CO)_3$ affords the spirocyclic compound $(\eta^1\text{-}Me_5C_5\overline{PN(t\text{-}Bu)}\underline{PN(t\text{-}Bu)C(O)Mo}(CO)_2(\eta^5\text{-}C_5Me_5)$ (5), whose structure was determined by X-ray crystallography. A metalloiminophosphane, $(\eta^5\text{-}Me_5C_5)(CO)_3MoP{=}N(t\text{-}Bu)$ (7), is proposed to be the key intermediate in the formation of 5.

The use of phosphorus(III) pπ systems as ligands in transition-metal complexes is well-established, and a vast number of such species is known.[1] Only recently this chemistry has been further expanded by incorporating organometallic substituents. New types of compounds include C- and P-metalated phosphaalkenes[2] and metallodiphosphenes,[3] as well as terminal and bridging phosphavinylidene complexes.[4] Here, we report on attempts to synthesize a metalloiminophosphane via the shift of a Me_5C_5 ligand from phosphorus to the transition metal, which has proven to be a convenient route to P-metalated phosphaalkenes.[5]

$Me_5C_5P{=}N(t\text{-}Bu)$ (1) was prepared in a two-step synthesis starting from $Me_5C_5PCl_2$ (2):[6] addition of 0.1 mol of $t\text{-}BuNH_2$ to a CH_2Cl_2 solution (200 mL) of 2 (0.1 mol) and Et_3N (0.1 mol) during 1 h at room temperature, filtration, and distillation gave the aminochlorophosphane 3.[7] Metalation of 3 (50 mmol) in THF at −70 °C (10 min), followed by elimination of LiCl on warming to −30 °C (1 h), produced 1. The product was purified by evacuation of the solvent, extraction of the residue with hexane, filtration, and distillation. 1 was obtained as a yellow, thermally stable liquid that could be identified on the basis of analytical and spectroscopic data.[8] Reaction of 1 with $(MeCN)_3Mo(CO)_3$ (4)[9] was found to proceed in a 2:1 molar

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(7) **3**: bp 80–90 °C (0.1 torr); yield 75–80%; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 28 °C) δ 142.9 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 28 °C) δ 10.9 (br) and 14.8 (br) H_3CC (ring), 31.4 (d, 9.3 Hz, $NCCH_3$), 51.5 (d, 12.1 Hz, NC), 62.0 (br, (PC ring), 136.7 (br, C ring); ^{1}H NMR ($CDCl_3$, 28 °C) δ 2.87 (br d, 15.4 Hz, 1 H, NH), 1.9–1.7 (br m, 15 H, CCH_3 ring), 1.09 (d, 1.1 Hz, 9 H, $NCCH_3$). Anal. Calcd for $C_{14}H_{25}ClNP$: C, 61.42; H, 9.20; N, 5.11. Found: C, 61.24; H, 9.31, N, 5.15.

(8) **1**: bp 50–54 °C (0.1 torr); yield 72–75%; MS (EI, 70 eV), *m/e* (relative intensity) 237 (10, M^+). $^{31}P\{^1H\}$ NMR (C_6D_6, 28 °C) δ 283.2 (s); $^{13}C\{^1H\}$ NMR (C_6D_6, 28 °C) δ 10.6 (d, 0.9 Hz, CCH_3 ring), 34.4 (d, 10.4 Hz, $NCCH_3$), 59.2 (s, NC), 124.1 (d, 5.3 Hz, C ring); ^{1}H NMR (C_6D_6, 28 °C) δ 1.39 (d, 1.4 Hz, 9 H, $NCCH_3$), 1.81 (d, 1.5 Hz, 15 H, CCH_3 ring). Anal. Calcd for $C_{14}H_{24}NP$: C, 70.85; H, 10.19; N, 5.90. Found: C, 69.33; H, 9.99; N, 5.72.

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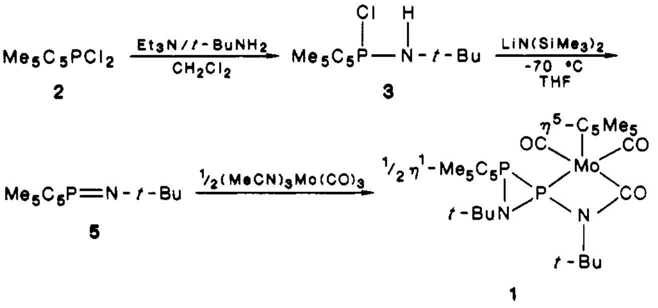


ratio. In a typical preparation, 4.0 mmol of 1, dissolved in 10 mL of CH$_2$Cl$_2$, was added to 2.0 mmol of 4 at 0 °C. The mixture immediately turned red-brown, and after stirring for 2 h at 20 °C, 4 dissolved completely. ^{31}P{^{1}H} NMR spectroscopy revealed four lines of an AB pattern (δ_A −20.3, δ_B −42.5, J_{AB} = 163.4 Hz, H$_3$PO$_4$ external) as the only detectable signals. After removal of volatiles, the residue was extracted with 20 mL of hexane and filtered. Concentration of the filtrate yielded an orange solid which was recrystallized once from hexane (mp 142–144 °C; yield 8–10%). Identification of the product as the spirocyclic 5 was established by analytical and spectroscopic data[10] and X-ray crystallography.[11] Though being thermally stable and only moderately air-sensitive in the solid state, 5 decomposes in solution within several hours at room temperature to yield a brown, viscous oil of yet unknown composition after workup.

The structure of 5 is illustrated in Figure 1. The 4-membered ring of the spirocyclic system is planar, and the two rings enclose a dihedral angle of 102°. P(1)–P(2) and P(2)–N(1) distances in the 3-membered ring are similar to the values reported for azadiphosphiridines,[12] while the P(1)–N(1) distance is shortened significantly. The P(1)–Mo bond length falls in the range of molybdenum-phosphine complexes (2.40–2.57 Å)[13] and the exocyclic P(1)–N(2) distance corresponds to a single bond. Both nitrogen atoms are planar within experimental error. Hence, the structure of 5 may be described as a transition-metal complex of an aminoaza-λ^3,λ^3-diphosphiridine.

Based on our results on cyclopentadienyl shift reactions of phosphaalkenes,[5] we propose the following mechanism for the formation of 2: reaction of the iminophosphane 1 with 4 initially produces the complex 6, which rearranges to form a metalloiminophosphane, 7. For the final formation of 5 from 7 two alternative routes may be discussed, viz., (i) [2 + 1] cycloaddition of 7 with a second molecule of 1,[14] followed by intramolecular attack of the imino nitrogen of the resulting aza-λ^5,λ^3-diphosphiridine on a CO ligand,[15] or (ii) isomerization of 7 to the cyclic phosphinidene complex 8 and subsequent oxidative addition of 1.[16]

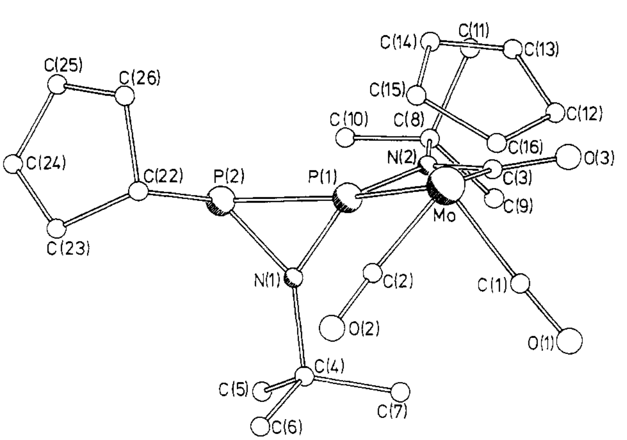
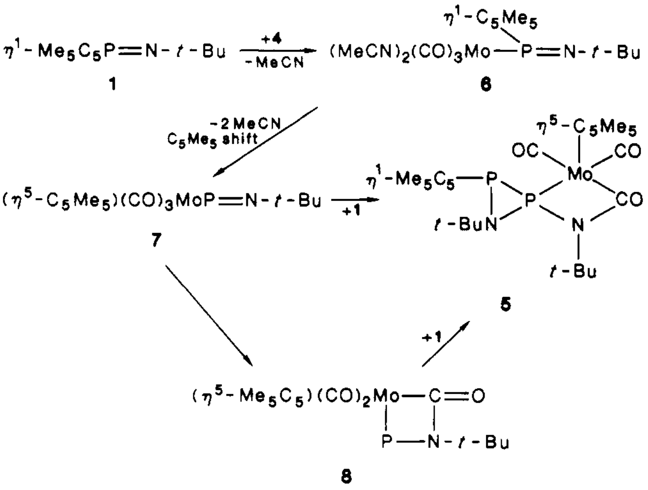


Figure 1. Drawing of (Me$_5$C$_5$)PN(*t*-Bu)PN(*t*-Bu)C(O)Mo(C$_5$Me$_5$)(CO)$_2$ (5) showing the atom numbering scheme. Methyl groups of the Me$_5$C$_5$ rings are omitted for clarity. Important structural parameters are as follows: P(1)–P(2) = 2.195 (9), P(1)–N(1) = 1.61 (2), P(1)–N(2) = 1.75 (2), P(1)–Mo = 2.449 (8), P(2)–N(1) = 1.71 (2), N(2)–C(3) = 1.39 (3), Mo–C(3) = 2.21 Å; P(2)–P(1)–N(1) = 50.4 (7), P(1)–P(2)–N(1) = 46.8 (6), P(1)–N(1)–P(2) = 82.8 (9)°.



Further study of the reactivity of Me$_5$C$_5$-substituted phosphaalkenes and iminophosphanes toward transition-metal complexes is in progress.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. D. Böhler, Universität Göttingen, for performing the FD-mass spectra.

Registry No. 1, 104324-90-5; 2, 61861-06-1; 3, 104324-91-6; 4, 15038-48-9; 5, 104335-72-0; *t*-BuNH$_2$, 75-64-9.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for 5 (6 pages); a listing of structure factors for 5 (10 pages). Ordering information is given on any current masthead page.

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(10) 5: FD-MS, *m/e* (relative intensity) 656 (100, M$^+$), 237 (94, C$_{14}$H$_{24}$NP$^+$); ^{1}H NMR (C$_6$C$_6$, 28 °C) δ 1.29 (s, 9 H) and 1.51 (s, 9 H) (NCCH$_3$), 1.74 (d, 1.7 Hz, 15 H) and 1.94 (d, 1.1 Hz, 15 H) (CCH$_3$ ring); IR (Nujol mull) ν(CO) 1934 (vst), 1862 (vst), 1618 (st) cm^{-1}. Anal. Calcd for C$_{31}$H$_{48}$MoN$_2$O$_3$P$_2$: C, 56.88; H, 7.39; N, 4.28. Found: C, 54.81; H, 7.51; N, 4.18.

(11) A single crystal of 5 with dimensions 0.03 × 0.1 × 0.25 mm was cooled to −133 °C with dry nitrogen. Some crystal data for 5 are as follows: C$_{31}$H$_{48}$MoN$_2$O$_3$P$_2$, M_r 654.7, orthorhombic, space group $P2_12_12_1$; a = 12.219 (7) Å), b = 16.891 (10) Å, c 15.768 (10) Å; V = 3258.1 Å^3; Z = 4; D(calcd) = 1.33 g cm^{-3}. A total of 2890 independent reflections were recorded (2θ–θ scan) in the range 4° < 2θ < 48° by using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Of these, 1692 reflections ($I > 1.96\sigma(I)$) were used to solve (Patterson; C, O, P, and N atoms from E map) and refine (full-matrix, least squares) the structure. Anomalous dispersion corrections were not applied. Final least-squares refinement gave R = 0.089 and R_w = 0.079.

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