Communications

Reaction of
(Pentamethylcyclopentadieny)l{(t-But-butydimino)phosphane with
Trit(4-tert-butydimino)tricarbonylmolybdenum(0);
Evidence for a Metalloiminophosphane Intermediate

Dietrich Gudat and Edgar Niecke*  
Fakultät für Chemie der Universität, Postfach 8840
D-4800 Bielefeld, West Germany

Bernt Krebs and Mechtild Dartmann  
Anorganisch Chemisches Institut der Universität
Giesvenbecker Weg 9, D-4400 Münster, West Germany

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Summary: (η^1-Me5CsP=Cl(t-Bu) (1) was prepared in a two-step synthesis from Me5CsPCl2. Reaction of 1 with
(MeCN)2Mo(CO)5 affords the spirocyclic compound (η^1-
Me5CsPN(t-Bu)PN(t-Bu)C(O)Mo(CO)5)(η^6-C6Me3) (5),
whose structure was determined by X-ray crystallography. A metalloiminophosphane, (η^5-Me5Cs)(CO)5MoP==N(t-Bu)
(7), is proposed to be the key intermediate in the formation of 5.

The use of phosphorus(III) pr systems as ligands in transition-metal complexes is well-established, and a vast
number of such species is known. Only recently this chemistry has been further expanded by incorporating organometallic substituents. New types of compounds include C- and P-metalated phosphainokenes and metal-

lodiphosphenes, as well as terminal and bridging phos-
phavinylidene complexes. Here, we report on attempts to synthesize a metalloiminophosphane via the shift of a Me5Cs ligand from phosphorus to the transition metal, which has proven to be a convenient route to P-metalated phosphainokenes.

Me5CsPN==N(t-Bu) (1) was prepared in a two-step synthesis starting from Me5CsPCl2 (2). Addition of 0.1 mol
of t-BuNH2 to a CH2Cl2 solution (200 mL) of 2 (0.1 mol) and Et3N (0.1 mol) during 1 h at room temperature,
fractionation, and distillation gave the aminochlorophosphane 3. 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. I was obtained as a yellow, thermally stable liquid that could be identified on the basis of analytical and spectroscopic data. Reaction of 1 with
(MeCN)2Mo(CO)5 (4) was found to proceed in a 2:1 molar

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(7) b: bp 80-90°C (0.1 torr); yield 76-80%; 1H NMR (CDCl3, 28°C) δ 4.29 (s); 3H NMR (CDCl3, 28°C) δ 10.9 (br) and 14.8 (br)
H2CC (ring); 1.4 (d, 2.3 Hz, CCH3), 1.3 (d, 12.1 Hz, NCCCH3), 62.6 (br, PC ring), 136.7 (br, C ring); 1H NMR (CDCl3, 28°C) δ 2.87 (br d, 15.4 Hz, 1 H, N, 1 H, NH), 1.9-1.7 (br m, 16 H, CCH3 ring), 1.0-9 (d, 1.1 Hz, 9 H, NCCCH3).
Anal. Calcd for C15H10CNP: C, 61.45; H, 5.26; N, 5.15. Found: C, 61.54; H, 5.31; N, 5.15.
(8) b: bp 80-94°C (0.1 torr); yield 75-78%; MS (EI, 70 eV), m/z (relative intensity) 237 (10, M+), 193 (100), 115 (10), 106 (100, CCH3), 58.2 (N, 124.1 (d, 5.5 Hz, C ring); 1H NMR (CDCl3, 28°C) δ 1.98 (d, 1.4 Hz, NCCCH3), 1.81 (d, 1.5 Hz, 15 H, CCH3 ring). Anal. Calcd for C24H18N: C, 70.85; H, 10.19; N, 5.90. Found: C, 69.33; H, 9.99; N, 5.72.
ratio. In a typical preparation, 4.0 mmol of 1, dissolved in 10 mL of CH₂Cl₂, was added to 2.0 mmol of N₂ at 0 °C. The mixture immediately turned red-brown, and after stirring for 2 h at 20 °C, 4 dissolved completely. P(1H) NMR spectroscopy revealed four lines of an AB pattern \( (\delta = -20.3, \delta_4 = -42.5, J_{AB} = 163.4 \text{ Hz}, H_2P(O)_{\text{ex}} \text{ external}) \) 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 spiroyclic 5 was established by analytical and spectroscopic data\(^{(9)}\) and X-ray crystallography.\(^{(9)}\) Though being thermally air-sensitive and only moderately 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 spiroyclic 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 azaphosphorines,\(^{(10)}\) while the P(1)-Mo bond length falls in the range of molybdenophosphine complexes (2.40–2.57 Å)\(^{(9)}\) 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 aminocyclo-\(\lambda^4,\lambda^3\)-diphosphorine.

Based on our results on cycloptadinyl shift reactions of phosphaalenes,\(^{(9)}\) we propose the following mechanism for the formation of 2: reaction of the iminophosphate 1 with 4 initially produces the complex 6, which rearranges to form a metallomimophosphine, 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 nitrogem.

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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.

(10) 6: FD-MS, m/e (relative intensity) 656 (100, M⁺), 257 (94), C₃H₇N₂O₃P⁺; 1H NMR (CDCl₃, 25 °C) δ 1.29 (s, 9 H) and 1.61 (s, 9 H) (NCH₃), 1.7 (d, 1.7 Hz, 15 H) and 1.94 (d, 1.1 Hz, 15 H) (CH₂CH₃ ring), IR (Nujol mull) ν(CO) 1994 (est), 1862 (est), 1618 (est) cm⁻¹. Anal. Calcd. for C₄H₇N₂O₃P: C, 56.88; H, 7.36; N, 4.28. Found: C, 54.81; H, 7.25; 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: C₆H₅MoN₂O₂P, M, 655.7, orthorhombic, space group P2₁2₁2₁, \( a = 12.219(7) \text{ Å}, b = 18.891(10) \text{ Å}, c = 17.768(10) \text{ Å}, V = 3285.3 \text{ Å³}, \), \( \alpha = 90.0, \beta = 90.0, \gamma = 90.0 \text{ Å}, \) \( D_{calc} = 1.33 \text{ g cm}^{-3}. \) A total of 2890 independent reflections were recorded (2θ max) in the range \( 4° < 2θ < 48° \) by using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Of these, 1029 reflections \( I > 1.6σ(I) \) 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 \( R_w = 0.079. \)
(15) A similar reaction of a coordinated iminophosphine was recently reported: Arif, A. M.; Cowley, A. H.; Pakulski, M. J. Am. Chem. Soc. 1986, 107, 5355.