

Communications

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

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Summary: $(\eta^1\text{-Me}_5\text{C}_5)\text{P}=\text{N}(t\text{-Bu})$ (**1**) was prepared in a two-step synthesis from $\text{Me}_5\text{C}_5\text{PCl}_2$. Reaction of **1** with $(\text{MeCN})_3\text{Mo}(\text{CO})_3$ affords the spirocyclic compound $(\eta^1\text{-Me}_5\text{C}_5\text{PN}(t\text{-Bu})\text{PN}(t\text{-Bu})\text{C}(\text{O})\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5))$ (**5**),

whose structure was determined by X-ray crystallography. A metalloiminophosphane, $(\eta^5\text{-Me}_5\text{C}_5)(\text{CO})_3\text{MoP}=\text{N}(t\text{-Bu})$ (**7**), is proposed to be the key intermediate in the formation of **5**.

The use of phosphorus(III) $p\pi$ 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 phosphalkenes² and metal-

lodiphosphenes,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 phosphalkenes.⁵

$\text{Me}_5\text{C}_5\text{P}=\text{N}(t\text{-Bu})$ (**1**) was prepared in a two-step synthesis starting from $\text{Me}_5\text{C}_5\text{PCl}_2$ (**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 $(\text{MeCN})_3\text{Mo}(\text{CO})_3$ (**4**)⁹ was found to proceed in a 2:1 molar

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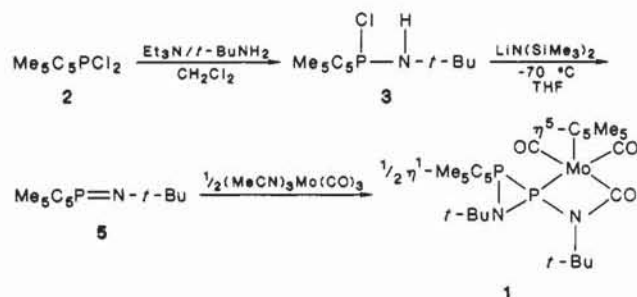
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(7) **3**: bp $80\text{--}90^\circ\text{C}$ (0.1 torr); yield 75–80%; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 28°C) δ 142.9 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 28°C) δ 10.9 (br) and 14.8 (br) H_3CC (ring), 31.4 (d, 9.3 Hz, NCCH_3), 51.5 (d, 12.1 Hz, NC), 62.0 (br, (PC ring), 136.7 (br, C ring); ^1H 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 $\text{C}_{14}\text{H}_{25}\text{ClNP}$: C, 61.42; H, 9.20; N, 5.11. Found: C, 61.24; H, 9.31; N, 5.15.

(8) **1**: bp $50\text{--}54^\circ\text{C}$ (0.1 torr); yield 72–75%; MS (EI, 70 eV), m/e (relative intensity) 237 (10, M^+). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 28°C) δ 283.2 (s); $^{13}\text{C}\{^1\text{H}\}$ 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); ^1H 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 $\text{C}_{14}\text{H}_{24}\text{NP}$: 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_2Cl_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. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed four lines of an AB pattern ($\delta_{\text{A}} -20.3$, $\delta_{\text{B}} -42.5$, $J_{\text{AB}} = 163.4$ Hz, H_3PO_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 data¹⁰ 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 phosphalkenes,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 ni-

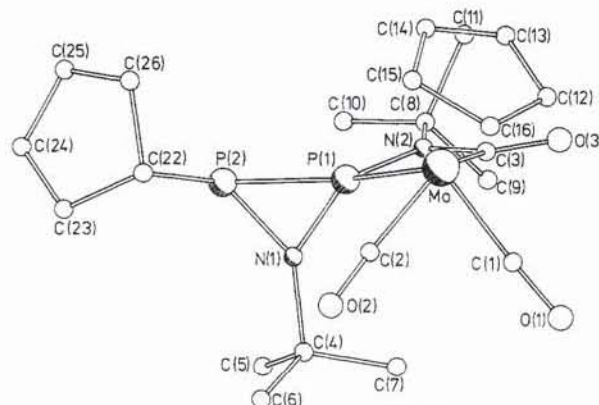
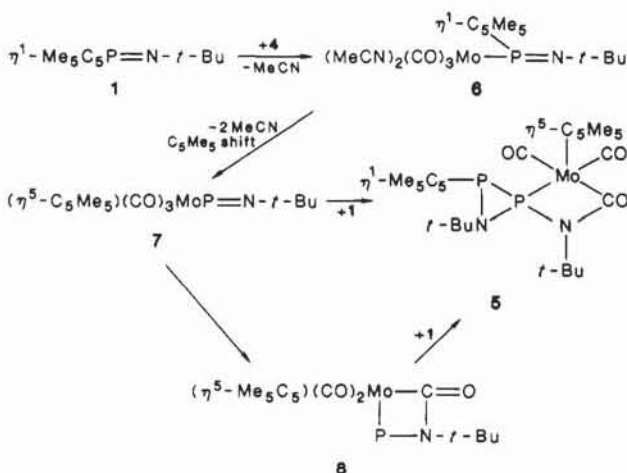


Figure 1. Drawing of $(\text{Me}_5\text{C}_5)\text{PN}(t\text{-Bu})\text{PN}(t\text{-Bu})\text{C}(\text{O})\text{Mo}(\text{C}_5\text{Me}_5)(\text{CO})_2$ (5) showing the atom numbering scheme. Methyl groups of the Me_5C_5 rings are omitted for clarity. Important structural parameters are as follows: 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)°.

trogen 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



Further study of the reactivity of Me_5C_5 -substituted phosphalkenes and iminophosphanes toward transition-metal complexes is in progress.

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Registry No. 1, 104324-90-5; 2, 61861-06-1; 3, 104324-91-6; 4, 15038-48-9; 5, 104335-72-0; *t*-BuNH₂, 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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(9) Tate, D. P.; Knipple, W. R.; Augl, I. M. *Inorg. Chem.* 1962, 1, 433.

(10) 5: FD-MS, *m/e* (relative intensity) 656 (100, M^+), 237 (94, $\text{C}_{14}\text{H}_{24}\text{NP}^+$); ^1H NMR (C_6D_6 , 28 °C) δ 1.29 (s, 9 H) and 1.51 (s, 9 H) (NCCCH_3), 1.74 (d, 1.7 Hz, 15 H) and 1.94 (d, 1.1 Hz, 15 H) (CCH_3 ring); IR (Nujol mull) $\nu(\text{CO})$ 1934 (vst), 1862 (vst), 1618 (st) cm^{-1} . Anal. Calcd for $\text{C}_{31}\text{H}_{48}\text{MoN}_2\text{O}_3\text{P}_2$: 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 $0.03 \times 0.1 \times 0.25$ mm was cooled to -133 °C with dry nitrogen. Some crystal data for 5 are as follows: $\text{C}_{31}\text{H}_{48}\text{MoN}_2\text{O}_3\text{P}_2$, M , 654.7, orthorhombic, space group $P2_12_12_1$; $a = 12.219$ (7) Å, $b = 16.891$ (10) Å, $c = 15.768$ (10) Å; $V = 3258.1$ Å³; $Z = 4$; $D(\text{calcd}) = 1.33$ g cm^{-3} . A total of 2890 independent reflections were recorded (2θ - θ scan) in the range $4^\circ < 2\theta < 48^\circ$ by using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ 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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