

Transfer of a Pentamethylcyclopentadienyl Ligand from Phosphorus to Nickel: Generation and Spectroscopic Characterization of the First Examples of Metalloiminophosphanes $[(\eta^5\text{-Me}_5\text{C}_5)(\text{R}_3\text{P})\text{Ni}-\text{P}=\text{NBU}^t]$ (R = Et, Bu, or Ph)

D. Gudat and E. Niecke*

Fakultät für Chemie der Universität, Postfach 8640, D-4800 Bielefeld, F.R.G.

Reaction of $(\text{Me}_5\text{C}_5)\text{P}=\text{NBU}^t$ with $[(\text{R}_3\text{P})_2\text{Ni}(\text{cod})]$ (cod = cyclo-octa-1,5-diene) (R = Et, Bu, or Ph) produces complexes $[(\text{R}_3\text{P})_2\text{Ni}(\text{C}_5\text{Me}_5)\text{P}=\text{NBU}^t]$, which rearrange to yield the novel metal-substituted iminophosphanes, $[(\text{R}_3\text{P})(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}-\text{P}=\text{NBU}^t]$ and free phosphane R_3P , the new complexes being identified by means of n.m.r. spectroscopy; similarly, the metallophospha-alkenes, $[(\text{R}_3\text{P})(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}-\text{P}=\text{C}(\text{SiMe}_3)_2]$ are formed *via* reaction of $(\text{Me}_5\text{C}_5)\text{P}=\text{C}(\text{SiMe}_3)_2$ and $[(\text{R}_3\text{P})\text{Ni}(\text{alkene})_2]$.

Incorporation of organometallic substituents is of current interest in the chemistry of phosphorus π -bonded systems, and a variety of transition metal-substituted phospho-alkenes and diphosphenes are known.¹⁻³ Three main synthetic routes give access to these compounds: (i) formation of a double bond in the co-ordination sphere of a transition metal *via* trimethylsilyl- or acylphosphido-complexes,¹ (ii) nucleophilic substitution of *P*-chlorophospha-alkenes with carbonyl-metalate anions,² and (iii) rearrangement of complexes of Me_5C_5 -substituted phospho-alkenes with transfer of the Me_5C_5 ligand from phosphorus to a metal centre.³ Recently it has been shown that cyclopentadienyl-transfer reactions may be extended to the synthesis of metal-substituted $\text{P}-\text{N}-\pi$ -systems. Thus, a $[2 + 1]$ cycloadduct of a transient metalloiminophosphane was isolated in the reaction of $(\text{Me}_5\text{C}_5)\text{P}=\text{NBU}^t$ (**1**) with a molybdenum carbonyl complex.⁴ Here we report on the generation and spectroscopic characterization of the first metalloiminophosphanes and d^{10} -transition metal-substituted phospho-alkenes, starting from the cyclopentadienyl-substituted precursors, $(\text{Me}_5\text{C}_5)\text{P}=\text{NBU}^t$ (**1**)⁴ and $(\text{Me}_5\text{C}_5)\text{P}=\text{C}(\text{SiMe}_3)_2$ (**2**),^{3a} and alkene complexes of nickel(0).

Reaction of (**1**) with one equivalent of $[(\text{Bu}_3\text{P})_2\text{Ni}(\text{cod})]$ (cod = cyclo-octa-1,5-diene),⁵ or a 2:1 mixture of R_3P and $\text{Ni}(\text{cod})_2$ (R = Et or Ph),[†] respectively, at -30°C in toluene (1–2 h) cleanly produced deep red solutions of iminophosphane complexes $[(\text{R}_3\text{P})_2\text{Ni}(\text{C}_5\text{Me}_5)\text{P}=\text{NBU}^t]$, which were identified by their $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra.[‡] In the case of R = Ph, the AX₂-pattern and the deshielding of the sp^2 -phosphorus nucleus indicate σ -co-ordination of the iminophosphane ligand⁶ (**3a**) (Scheme 1). For R = Et or Bu, the n.m.r. spectra reveal the presence of two components in a 1:3 (R = Et) and 3:7 (R = Bu) ratio. The species of minor occurrence again may be considered as σ -co-ordinated complexes (**3b,c**). The main components exhibit ABX-type spectra and chemical

shifts characteristics of complexes of η^2 -co-ordinated iminophosphanes^{6b} and are thus attributed to π -complexes (**4b,c**) (Scheme 1).

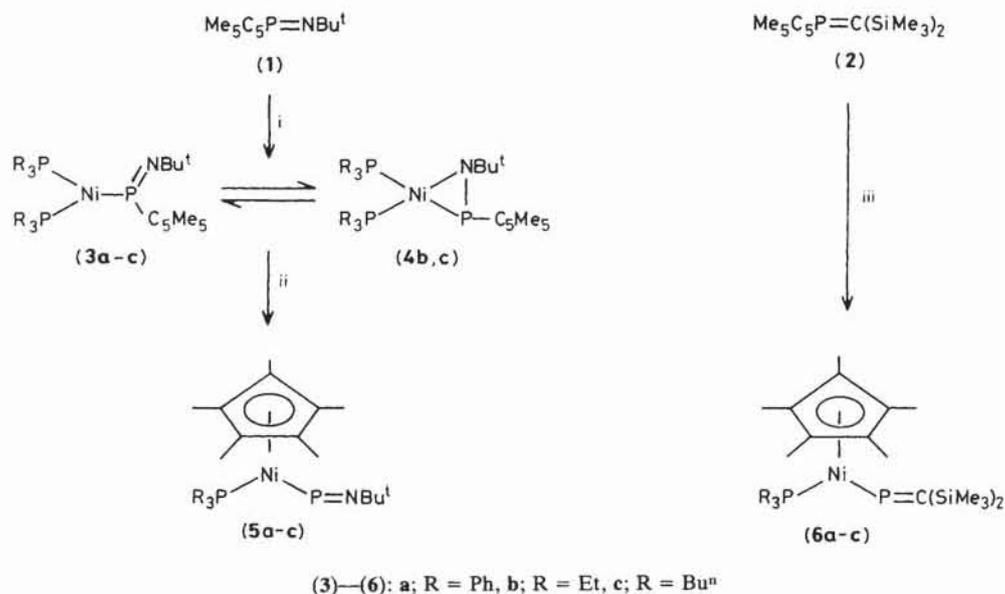
On warming above -5°C , solutions of (**3**) and (**4**) were found to change colour to red-brown. Concomitantly, new resonances appeared in the ^{31}P n.m.r. spectra, which are attributable to free phosphane, R_3P , and the novel metalloiminophosphanes, $[(\text{R}_3\text{P})(\eta^5\text{-C}_5\text{Me}_5)\text{Ni}-\text{P}=\text{NBU}^t]$ (**5a-c**)[‡] (Scheme 1). The signals of complexes (**3**) and (**4**) completely disappeared within 1 h at room temperature, and formation of metalloiminophosphanes is almost quantitative (>95%) in the case of trialkylphosphane-substituted species (**5b,c**). Compound (**5a**) (R = Ph), in contrast, is rapidly decomposed even at low temperatures, only polymeric products and free triphenylphosphane being observed in the ^{31}P n.m.r. spectrum after 30 min at ambient temperature. Solutions of (**5b,c**) were stable for several hours at room temperature with excess free ligand present. Removal of solvent and excess phosphane *in vacuo*, however, accelerated decomposition to yield polymeric products, which have so far prevented work-up of the reaction mixtures and isolation of pure compounds.

However, unambiguous characterization was possible by means of n.m.r. spectroscopy.[§] The extreme deshielding of the low-field ^{31}P signal of the AX-spectra of (**5a-c**) (δ 753–768 p.p.m.) indicates a transition metal-substituted phosphorus π -system.^{2,3} The phosphorus-phosphorus coupling constant falls in the range reported for 18e Ni^0 complexes (0–40 Hz).⁷ The ^1H n.m.r. spectra, beside the resonances of

† The main components present in mixtures of $\text{R}_3\text{P}/\text{Ni}(\text{cod})_2$ (2:1) or $\text{R}_3\text{P}/\text{Ni}(\text{cod})_2$ (1:1)/ C_2H_4 may be regarded as $[(\text{R}_3\text{P})_2\text{Ni}(\text{cod})]$ and $[(\text{R}_3\text{P})\text{Ni}(\text{alkene})_2]$, respectively; see ref. 5 and P. W. Jolly, I. Tkatchenko, and G. Wilke, *Angew. Chem.*, 1971, **83**, 328; *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 326.

‡ $^{31}\text{P}\{^1\text{H}\}$ N.m.r. (32.2 MHz, p.p.m. from ext. H_3PO_4 , in $\text{CD}_3\text{C}_6\text{D}_5$ or C_6D_6): (**3a**) (-20°C), P_a 26.8 (d), P_b 325.3 (t), J_{ab} 96 Hz; (**3b**) (-10°C), P_a 11.1 (d), P_b 314.5 (t), J_{ab} 105 Hz; (**3c**) (-30°C), P_a 3.0 (d), P_b 312.0 (t), J_{ab} 107 Hz; (**4b**) (-10°C): P_a 10.2 (dd), P_b 14.0 (dd), P_c 73.7 (d, br.), J_{ab} 24.4, J_{ac} 27.0, J_{bc} 1.2 Hz; (**4c**) (-30°C), P_a 2.7 (dd), P_b 7.2 (dd), P_c 73.6 (dd), J_{ab} 26.8, J_{ac} 29.2, J_{bc} 3.5 Hz; (**5a**) P_a 51.4, P_b 752.0; (**5b**) P_a 35.5 (d), P_b 767.5 (br.), J_{ab} 1.4 Hz; (**5c**) P_a 27.4 (d), P_b 768.4 (br.), J_{ab} 1.3 Hz; (**6a**) P_a 39.2 (d), P_b 722.5 (d), J_{ab} 35.0 Hz; (**6b**) P_a 17.7 (d), P_b 740.5 (d), J_{ab} 21.3 Hz; (**6c**) P_a 10.3 (d), P_b 740.2 (d), J_{ab} 23.4 Hz.

§ $^{13}\text{C}\{^1\text{H}\}$ N.m.r. (75.1 MHz, int. SiMe_4 , in C_6D_6): (**5b**) δ 7.9 (s, PCH_2CH_3), 10.1 [d, J 7.3 Hz, CCH_3 (ring)], 12.3 (dd, $^1J_{\text{PC}}$ 27.9, $^3J_{\text{PC}}$ 1.6 Hz, PCH_2), 33.5 (d, J 11.0 Hz, PNCCH_3), 65.1 (s, PNC), 100.2 [d, J 0.9 Hz, C (ring)]; (**5c**) δ 10.3 [d, J 7.9 Hz, CCH_3 (ring)], 13.9 (s, PCCCCH_3), 19.9 (dd, $^1J_{\text{PC}}$ 27.6, $^3J_{\text{PC}}$ 1.6 Hz, PCH_2), 24.4 (d, J 12.8 Hz, PCCCCH_3), 26.6 (s, PCCH_3), 33.8 (d, J 11.0 Hz, PNCCH_3), 65.3 (s, PNC), 100.3 [d, J 0.9 Hz, C (ring)]; (**6a**) δ 2.9 (s, SiCH_3) and 3.9 (d, J 11.6 Hz, SiCH_3), 10.0 [s, CCH_3 (ring)], 100.9 [s, C (ring)], 128.8 [s, C-3,5(Ph)], 129.5 [s, C-4 (Ph)], 134.0 [d, J 41.5 Hz, C-1(Ph)], 134.5 [d, J 11.3 Hz C-2,6(Ph)], 203.7 (dd, $^1J_{\text{PC}}$ 109.8, $^3J_{\text{PC}}$ 3.0 Hz, P=C). (**6b**) δ 2.8 (d, J 1.6 Hz, SiCH_3), 3.7 (d, J 13.0 Hz, SiCH_3), 7.5 (br., PCCH_3), 10.1 [d, J 5.1 Hz, CCH_3 (ring)], 16.9 (dd, $^1J_{\text{PC}}$ 25.6, $^3J_{\text{PC}}$ 3.0 Hz, PCH_2), 99.5 [d, J 1.1 Hz, C (ring)], 207.0 (d, J 112.8 Hz, P=C); (**6c**) δ 2.9 (s, SiCH_3), 3.7 (d, J 12.7 Hz, SiCH_3), 10.2 [d, J 5.8 Hz, CCH_3 (ring)], 14.0 (s, PCCCCH_3), 24.7 (d, J 12.5 Hz, PCCCCH_3), 25.2 (d, 25.0 Hz, PCH_2), 26.1 (s, PCCH_3), 99.5 [d, J 0.7 Hz, C (ring)], 206.7 (d, J 111.2 Hz, P=C). ^1H N.m.r. (300 MHz, SiMe_4 , C_6D_6): (**5b**) δ 1.50 (s, 9H, PNCCH_3), 1.83 [s, 15H, CCH_3 (ring)]; (**5c**) 1.56 (s, 9H, PNCCH_3), 1.89 [s, 15H, CCH_3 (ring)]; (**6a**) δ 0.32 (s, 9H, SiCH_3), 0.54 (s, 9H, SiCH_3), 1.56 [d, J 0.85, 15H, CCH_3 (ring)], 7.02 (m, 9H, PC_6H_5), 7.52 (m, 6H, PC_6H_5); (**6b**) δ 0.45 (s, 9H, SiCH_3), 0.66 (s, 9H, SiCH_3), 0.81 (m, br., 9H, PCCCCH_3), 1.15 (m, br., 6H, PCH_2), 1.71 [s, 15H, CCH_3 (ring)]; (**6c**) δ 0.47 (s, 9H, SiCH_3), 0.69 (s, 9H, SiCH_3), 0.88 (t, J_{HH} 6.8 Hz, PCCCCH_3), 1.28 (m, br., 12H, PCCH_2CH_2), 1.40 (m, 6H, PCH_2), 1.76, [s, 15H, CCH_3 (ring)].



Scheme 1. Reagents and conditions: i, $(\text{R}_3\text{P})_2\text{Ni}(\text{cod})$ (1 equiv.), toluene, -30°C , 2 h; ii, -20°C , 1 h; iii, $(\text{R}_3\text{P})\text{Ni}(\text{alkene})_2$ (1 equiv.), benzene, 25°C , 1 h.

free cyclo-octadiene, exhibit two singlets for the protons of the Bu^t - and C_5Me_5 -moieties, while the resonances of free and co-ordinated phosphane cannot be resolved. Direct evidence for the phosphorus-to-metal shift of the C_5Me_5 ligand is provided by ^{13}C n.m.r. data: the chemical shift of the ring carbons (δ 100) as well as the ^{13}C - ^{31}P coupling constants of the ring- ($^2J_{\text{PC}}$ 0.9 Hz) and methyl-carbon atoms ($^3J_{\text{PC}}$ 7–8 Hz) are in accord with values for C_5Me_5 ligands of metal-substituted phospho-alkenes and diphosphenes,^{1,3} but differ significantly from data of cyclopentadienyl substituents on phosphorus [δ $^{13}\text{C}(\text{ring})$ 124–125, $J_{\text{PC}}(\text{ring})$ 9–11, $J_{\text{PC}}(\text{methyl})$ 1–2 Hz].^{3a,4}

Further support for the constitution of (5a–c) as metal-substituted iminophosphanes is given by a similar synthesis of the corresponding phospho-alkenes. Thus, reaction of methylenephosphane (2) with an equimolar amount of a mixture of $\text{R}_3\text{P}/\text{Ni}(\text{cod})_2$ (1:1) in diethyl ether in the presence of ethylene† (20 – 30°C , 30 min) produced (6a–c) in 90–95% yield (by integration of ^{31}P n.m.r. spectra) (Scheme 1). Compound (6a) (R = Ph) could be isolated as dark brown crystals after evaporation of solvent and recrystallization from a small amount of diethyl ether [yield 35–40%, m.p. 114 – 119°C (decomp.)]. Crude (6b,c) remained after evaporation of all volatile material as red-brown, viscous oils which could not be further purified. Elucidation of the constitution of the products was again possible on the basis of n.m.r. data. In the $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra AX-patterns and a deshielding of the doubly co-ordinated P-atom, similar to the iminophosphanes (5), are observed (δ 722–741). The presence of a $\text{P}=\text{C}$ double bond is further indicated by the characteristic low-field ^{13}C -resonance (δ 203–207, $^1J_{\text{PC}}$ 110–112 Hz) and the typical inequivalence of the two Me_3Si substituents in both ^{13}C and

^1H n.m.r. spectra. § The resonances attributable to the carbon nuclei of the Me_5C_5 moiety correspond to the values found for (5b,c) and are in accord with a metal-bound five-membered ring.

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