Transfer of a Pentamethylcyclopentadienyl Ligand from Phosphorus to Nickel: Generation and Spectroscopic Characterization of the First Examples of Metalloiminophosphanes [(η^5-Me_5C_5)(R_3P)Ni–P=NBu^t] (R = Et, Bu, or Ph)

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Reaction of (Me_5C_5)P=NBu^t with [(R_3P)$_2$Ni(cod)] (cod = cyclo-octa-1,5-diene) (R = Et, Bu, or Ph) produces complexes [(R_3P)$_2$Ni(C_5Me_5)P=NBu^t], which rearrange to yield the novel metal-substituted iminophosphanes, [(R_3P)(η^5-C_5Me_5)Ni–P=NBu^t] and free phosphane R_3P, the new complexes being identified by means of n.m.r. spectroscopy; similarly, the metallophospha-alkenes, [(R_3P)(η^5-C_5Me_5)Ni–P=C($SiMe_3$)$_2$] are formed *via* reaction of (Me_5C_5)P=C($SiMe_3$)$_2$ and [(R_3P)Ni(alkene)$_2$].

Incorporation of organometallic substituents is of current interest in the chemistry of phosphorus pπ-bonded systems, and a variety of transition metal-substituted phospha-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 carbonylmetallate anions,[2] and (iii) rearrangement of complexes of Me_5C_5-substituted phospha-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 P–N-π-systems. Thus, a [2 + 1] cycloadduct of a transient metalloiminophosphane was isolated in the reaction of (Me_5C_5)-P=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 phospha-alkenes, starting from the cyclopentadienyl-substituted precursors, (Me_5C_5)P=NBu^t (**1**)[4] and (Me_5C_5)P=C($SiMe_3$)$_2$ (**2**),[3a] and alkene complexes of nickel(0).

Reaction of (**1**) with one equivalent of [(Bu_3P)$_2$Ni(cod)] (cod = cyclo-octa-1,5-diene),[5] or a 2 : 1 mixture of R_3P and Ni(cod)$_2$ (R = Et or Ph),† respectively, at −30 °C in toluene (1—2 h) cleanly produced deep red solutions of iminophosphane complexes [(R_3P)$_2$Ni(C_5Me_5)P=NBu^t], which were identified by their $^{31}P\{^1H\}$ n.m.r. spectra.‡ In the case of R = Ph, the AX_2-pattern and the deshielding of the sp^2-phosphorus nucleus indicate σ-co-ordination of the iminophosphane ligand[6] (**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, [(R_3P)(η^5-Me_5C_5)Ni–P=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 pπ-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

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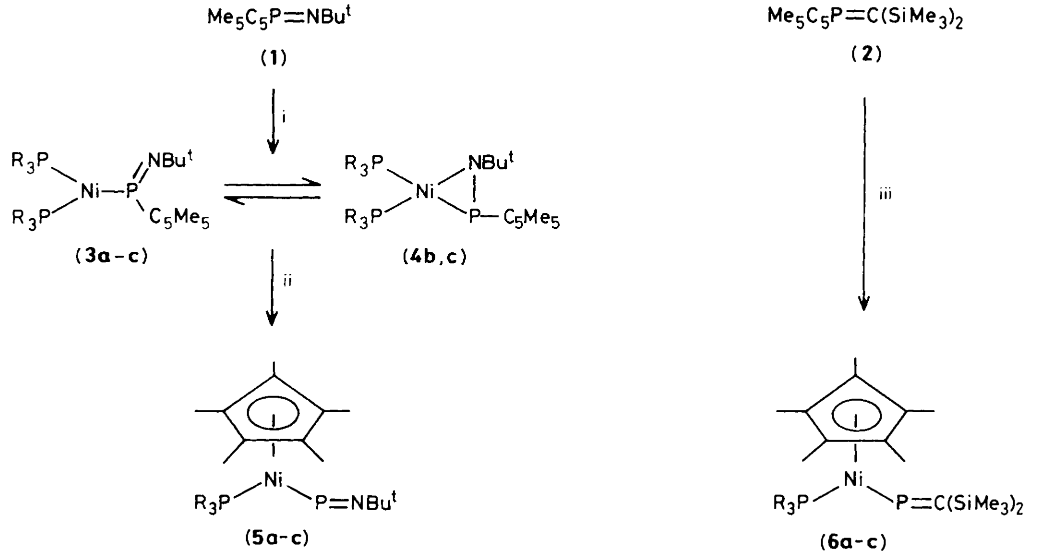
† The main components present in mixtures of R_3P/Ni(cod)$_2$ (2 : 1) or R_3P/Ni(cod)$_2$ (1 : 1)/C_2H_4 may be regarded as [(R_3P)$_2$Ni(cod)] and [(R_3P)Ni(alkene)$_2$], respectively; see ref. 5 and P. W. Jolly, I. Tkatchenko, and G. Wilke, *Angew. Chem.*, 1971, **83**, 328; *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 326.

‡ $^{31}P\{^1H\}$ N.m.r. (32.2 MHz, p.p.m. from ext. H_3PO_4, in $CD_3C_6D_5$ 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 2.1 (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.

§ $^{13}C\{^1H\}$ 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, $^1J_{PC}$ 27.9, $^3J_{PC}$ 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, $^1J_{PC}$ 27.6, $^3J_{PC}$ 1.6 Hz, PCH_2), 24.4 (d, *J* 12.8 Hz, $PCCCH_2$), 26.6 (s, $PCCH_2$), 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, $^1J_{PC}$ 109.8, $^3J_{PC}$ 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, $^1J_{PC}$ 25.6, $^3J_{PC}$ 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, $PCCCH_2$), 25.2 (d, 25.0 Hz, PCH_2), 26.1 (s, $PCCH_2$), 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, $PCCH_3$), 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)].



(**3**)—(**6**): **a**; R = Ph, **b**; R = Et, **c**; R = Bu^n

Scheme 1. *Reagents and conditions:* i, $(R_3P)_2Ni(cod)$ (1 equiv.), toluene, −30 °C, 2 h; ii, −20 °C, 1 h; iii, $(R_3P)Ni(alkene)_2$ (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- ($^2J_{PC}$ 0.9 Hz) and methyl-carbon atoms ($^3J_{PC}$ 7—8 Hz) are in accord with values for C_5Me_5 ligands of metal-substituted phospha-alkenes and diphosphenes,[1,3] but differ significantly from data of cyclopentadienyl substituents on phosphorus [δ ^{13}C(ring) 124—125, J_{PC}(ring) 9—11, J_{PC}(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 phospha-alkenes. Thus, reaction of methylenephosphane (**2**) with an equimolar amount of a mixture of $R_3P/Ni(cod)_2$ (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 $^{31}P\{^1H\}$ 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 P=C double bond is further indicated by the characteristic low-field ^{13}C-resonance (δ 203—207, $^1J_{PC}$ 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.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Received, 2nd September 1986; Com. 1261

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