Insertion of Terminal Phosphinidene Complexes into a Nickel–Carbon Bond; *X*-Ray Crystal Structure of the Complex $[\mathrm{CpNi}\{\eta\text{-Me-}\overline{\mathrm{P{-}CPh{=}CPh{-}Ni}}\mathrm{Cp}\}\mathrm{P{-}W(CO)_5}]$ (Cp = Cyclopentadienyl)

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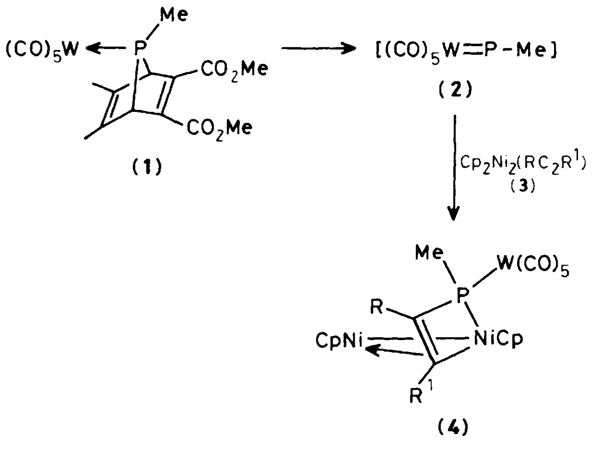
New phosphametallacyclobutene complexes (**4a–c**) have been obtained by the reactions of (7-methyl-7-phosphanorbornadiene)pentacarbonyltungsten (**1**) with some alkynebis(cyclopentadienylnickel) complexes.

In a series of recent papers, we have described the reactivity of terminal phosphinidene complexes [RP=W(CO)$_5$] [1] towards common organic compounds. Addition of the phosphinidene complexes to olefins[2] and alkynes,[1] and insertion reactions into N–H, O–H,[3] and strained N–C and O–C[4] bonds were observed. However, the behaviour of such phosphinidene complexes towards organometallic species is still almost unexplored: only the reactions between phosphinidenes and Fischer-type carbene complexes have been studied.[5] We report here a new reaction of terminal phosphinidene complexes (**2**) with $Cp_2Ni_2(C_2R_2)$ clusters. The transient species (**2**) is generated, as usual, from the corresponding 7-phosphanorbornadiene–$W(CO_5)$ complex (**1**) by thermolysis at 120 °C (method A) or at 60 °C with CuCl as catalyst (method B). It reacts with the bimetallic nickel alkyne complexes (**3**) to give the new phosphametallacyclobutene complexes (**4**).

According to the ^{31}P n.m.r. spectra of the crude reaction mixtures, the complexes (**4a—c**) are the only products formed. Purifications were performed by column chromatography on silica gel and crystallization. The phosphinidene complex (**2**) inserts selectively into the Ni–$C(CO_2Et)$ bond of (**3b**) and preferentially into the Ni–CH bond of (**3c**).

The structural formulation of the complexes (**4a—c**) was based on ^{31}P, ^{13}C, and ^{1}H n.m.r., i.r., and mass spectroscopic data† and confirmed by an *X*-ray diffraction study of (**4a**).‡



	R	R¹	Method	Yield (%)	$\delta(^{31}P)$ (J_{PW}/Hz)
a;	Ph	Ph	B	40	−113.4 (222)
b;	CO_2Et	Ph	A	42	−99.8 (229)
c;	H	Ph	B	25	−119.9 (217)
	Ph	H			−139.7

The adducts (**4a—c**) contain the $[MeP{\rightarrow}W(CO)_5]$ entity inserted into a Ni–C bond of the starting alkynebis(cyclopentadienylnickel) cluster. The co-ordination mode of the second nickel atom is unchanged. Similar phosphametallacyclobutene complexes are obtained otherwise by photochemical insertion of some alkynes into the P–Fe bond of the trimetallic phosphinidene cluster $(\mu_3\text{-PR})Fe_3(CO)_{10}$.[6] The insertion of ML_2 (M = Ni, Pd, or Pt; L = phosphine) into phosphirenes yields similar heterocycles.[7]

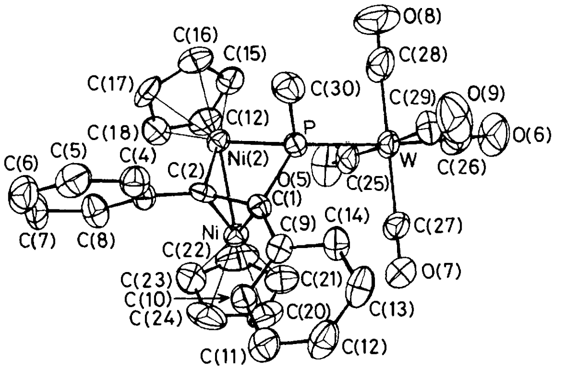


Figure 1. *X*-Ray crystal structure of $[CpNiW(CO)_5\{MeP\text{–}CPh{=}CPh\text{–}NiCp\}]$ (**4a**). Principal bond distances (Å): Ni(2)–P 2.197(2), P–C(1) 1.812(8), C(1)–C(2) 1.41(1), C(2)–Ni(2) 1.920(7), P–C(30) 1.843(9), P–W 2.532(2), Ni–Ni(2) 2.345(1), Ni–C(2) 1.876(8), Ni–C(1) 2.006(7). Bond angles (°) Ni(2)–P–C(1) 81.0(3), P–C(1)–C(2) 98.5(5), C(1)–C(2)–Ni(2) 102.5(5), C(2)–Ni(2)–P 72.9(2), Ni(2)–P–W 122.88(9), Ni(2)–P–C(30) 104.7(4), C(2)–Ni–C(1) 42.5(3), C(2)–Ni(2)–Ni 51.0(2).

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† (**4a**): ^{1}H n.m.r. (C_6D_6) δ 1.73 [d, ^{2}J(H–P) 5.1 Hz, Me], 4.92 (s, Cp), and 5.07 (s, Cp); ^{13}C n.m.r. ($CDCl_3$) δ 31.96 [d, ^{1}J (C–P) 8.0 Hz, Me], 70.69 [d, ^{1}J(C–P) 13.6 Hz, P *C*–Ph], 92.09 (Cp), 92.91 (Cp), 139.7 (d, *J* 7.5 Hz), 147.50, 153.89, 198.80 [d, ^{2}J(C–P) 6.5 Hz, *cis*-CO], and 200.55 [d, ^{2}J(C–P) 23.1 Hz, *trans*-CO]; i.r. (decalin) ν (CO) 2070m, 1935s, and 1930vs cm^{-1}; mass spectrum (70 eV; ^{58}Ni, ^{184}W) *m/z* 766 (*M*−CO, 8%), 710 (*M*−3CO, 21%), 654 (*M*−5CO, 13%), and 476 (*M*−5CO−C_2Ph_2, 100%)

(**4b**): ^{1}H n.m.r. (C_6D_6) δ 1.02 [t, ^{3}J(H–H) 7.0 Hz], 1.72 [d, ^{2}J(H–P) 5.6 Hz, PMe], 3.9 (m, CH_2), 4.86 (s, Cp), and 5.24 (s, Cp); ^{13}C n.m.r. ($CDCl_3$) δ 14.18 (CH_2CH_3), 31.31 [d, ^{1}J(C–P) 6.0 Hz, PMe], 57.03 [d, ^{1}J(C–P) 13.7 Hz, P–*C*–CO_2], 60.72 (CH_2), 91.99 (Cp), 93.03 (Cp), 128.33, 128.53, 129.18, 146.89, 160.13, 167.62 [d, ^{2}J(C–P) 7.5 Hz, CO_2Et], 198.69 [d, ^{2}J(C–P) 6.5 Hz, *cis*-CO], and 200.91 [d, ^{2}J(C–P) 25.7 Hz, *trans*-CO); i.r. (decalin) ν(CO) 2060m, 1940sh, and 1930vs cm^{-1}; ν(ester CO) 1700 cm^{-1}; mass spectrum (70 eV, ^{58}Ni, ^{184}W) *m/z* 762 (*M*−CO, 13%), 706 (*M*−3CO, 30%), 650 (*M*−5CO, 10%), and 476 (*M*−5CO−PhC_2CO_2Et, 100%).

(**4c**): mixture of two isomers, the major characterised as follows: ^{1}H n.m.r. (C_6D_6) δ 1.52 [d, ^{2}J(H–P) 5.4 Hz, Me], 3.74 [d, ^{2}J(H–P) 19.3 Hz, P–CH], 4.92 (s, Cp), and 5.09 (s, Cp); ^{13}C n.m.r. ($CDCl_3$) δ 34.43 (PMe), 52.13 [d, ^{1}J(C–P) 14.6 Hz, P*C*H), 91.01 (Cp), 92.27 (Cp), 128.60, 147.99, 159.51, and 198.86 [d, ^{2}J(C–P) 6.0 Hz, *cis* CO); Mass spectrum (70 eV, ^{58}Ni, ^{184}W) *m/z* 690 (*M*−CO, 6%), 662 (*M*−2CO, 17%), 634 (*M*−3CO, 38%), 578 (*M*−5CO, 32%), and 476 (*M*−5CO−PhC_2H, 100%).

‡ *Crystal data* for (**4a**): $C_{30}H_{23}O_5PNi_2W$, *M* = 795.76, orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 11.888(1), *b* = 14.479(1), *c* = 17.000(2) Å, *U* = 2926.2(8) Å^3, *Z* = 4, D_c = 1.806 g cm^{-3}, Mo-K_α (0.71073 Å) radiation, μ = 53.8 cm^{-1}, *F*(000) = 1552. Intensity data were collected with an Enraf-Nonius CAD4 diffractometer in the Θ–2Θ scan mode. The intensities of 4745 reflections were measured in the range 2° ≤ Θ ≤ 30°.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using the 2837 unique reflections having $F^2 > 3\,\sigma(F^2)$. The final $R_1(F)$ and $R_2(F)$ values are 0.032 and 0.034, respectively. The goodness of fit is 1.08. The enantiomeric structure yields *R* = 0.054. Atomic co-ordinates, bond and angle tables, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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