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Preliminary communication

COMPLEX FORMATION BETWEEN NICKEL(0) AND A PHOSPHAALKENE: INFLUENCE OF THE SECOND LIGAND ON THE η^1- AND η^2-COORDINATION MODE

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Summary

The η^2-complex (bipy)Ni(XyP=CPh_2) has been prepared and its structure determined by X-ray analysis. In contrast, $Ni(CO)_4$ forms η^1-complexes by replacement of one or two CO ligands by XyP=CPh_2.

One of the fascinating aspects of the novel phosphaalkenes [1] is their coordination chemistry. Calculations [2,3] and chemical experience [3] indicate that the phosphorus lone pair σ-orbital and the π-orbital of the P=C bond are the highest occupied molecular orbitals of nearly equal energy, and the level of the lowest unoccupied π^*-orbital is relatively low. One may therefore expect that phosphaalkenes on coordination to transition metal centers will exhibit either η^1-coordination via the lone pair or η^2-coordination of the Dewar—Chatt—Duncanson type via the P=C bond. The first mode of coordination has been established for chromium(0) [4,5], tungsten(0), rhodium(I) and platinum(II) [5] and for palladium(0) [6]. For platinum(0) we have observed a subtle equilibrium between the two modes of bonding [7]. A recent communication by Cowley et al. describes the formation of a η^2-complex of nickel(0) from nickel(II) by a remarkable redox reaction [8] (eq. 1).

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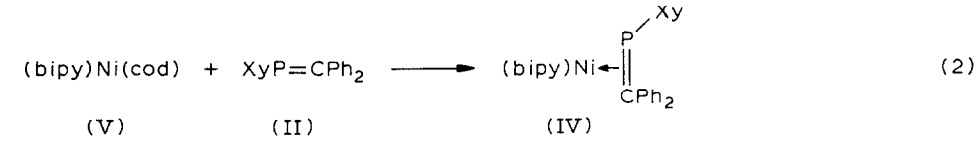
$$(Me_3P)_2NiCl_2 + 2\,Na[P\{CH(SiMe_3)_2\}_2] \rightarrow (Me_3P)_2Ni[(Me_3Si)_2CHP{=}C(SiMe_3)_2] \quad (1)$$

(I)

This prompts us to describe our investigations on the direct complex formation between nickel(0) and the triaryl-substituted phosphaalkenes II and III.

There is a large body of evidence suggesting that the second ligand on nickel has a strong influence on the factors operative in bonding to the first one [9]. In particular, one would expect that 2,2′-bipyridyl (bipy) as a weak π-acceptor should favour η^2-coordination of (bipy)Ni^0 because the "π-donating capacity" of the metal towards e.g. a phosphaalkene is little impaired. In contrast, CO, as a strong π-acceptor, should destabilize η^2-coordination of nickel(0) towards a phosphaalkene.

The complex 2,2′-bipyridyl(2,6-dimethylphenyl)(diphenylmethylene)-nickel(0) (IV) was obtained by slowly adding a solution of II (172.1 mg, 0.57 mmol) in THF (20 ml) to a solution of (bipy)Ni(cod) (V) (193.8 mg, 0.6 mmol) in THF (20 ml) at 20°C; the colour changed from blue-violet to grass-green. The resulting solution was concentrated to ca. 5 ml, and a few drops of ether were added. After several days, dark green, air-sensitive prisms of IV·THF separated (eq. 2).



(2)

(bipy = 2,2′-bipyridyl; cod = 1,5-cyclooctadiene; Xy = 2,6-dimethylphenyl)

The X-ray crystal structure determination* revealed the expected η^2-coordination of square planar nickel (Fig. 1). Of particular interest are the data for the three-membered ring Ni—P=C, showing the exceptionally long "P=C" bond of 1.832(6) Å; this value is typical of a P—C single bond rather than a P=C double bond, which is, for instance, 1.692(3) Å in mesityl(diphenylmethylene)phosphine (III) [3]; in $(CO)_5Cr$·III, a η^1-complex, the P=C bond length is practically unchanged: 1.679(4) Å [4]. The P=C bond in IV is longer and the Ni—P and Ni—C bonds shorter than in I. This indicates much stronger π-back bonding in IV compared to I. In fact, in IV the structure of a nickelaphosphacyclopropane seems to be more or less realized. The pyramidalization of the "alkene" atoms, which is typical for η^2-complexes, is clearly expressed by the torsional angles NiC(11)PC(24) 108.9(2)°, NiPC(11)C(18) 113.7(5)°, and NiPC(11)C(12) −94.3(4)°. Remarkably, the degree of back-bending differs

*Details of the structure determination of IV will be published elsewhere. The crystals were monoclinic with space group $P2_1/n$ and 4 formula units of IV and 4 molecules of tetrahydrofuran per unit cell of dimensions a 11.271(1), b 16.926(1), c 16.058(2) Å, β 96.21°. The final R value is 0.064. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

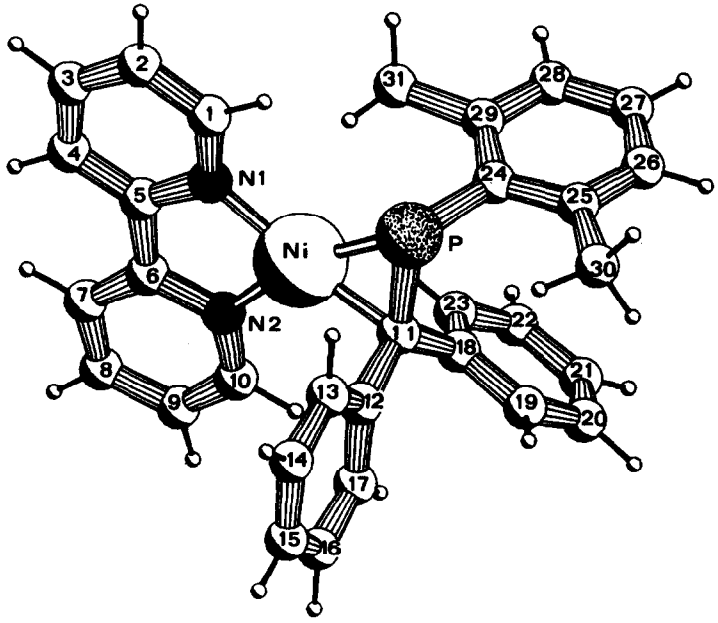


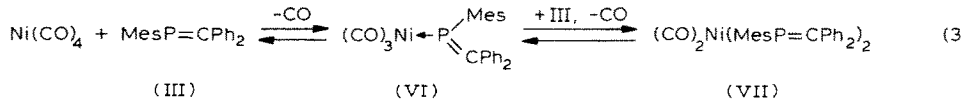
Fig. 1. PLUTO III drawing of (bipy)Ni(XyP=CPh$_2$) (IV), including the adopted numbering scheme. Selected bond lengths (Å), bond angles (°) and torsion angles (°) are: NiP 2.177(2), NiC(11) 1.987(6), NiN(1) 1.940(5), NiN(2) 1.951(5), PC(11) 1.832(6), PC(24) 1.845(6), C(11)C(12) 1.488(8), C(11)C(18) 1.491(8); PNiC(11) 52.0(2), N(1)NiN(2) 83.2(2), NiPC(11) 58.7(2), NiC(11)P 69.4(2), C(11)PC(24) 102.6(3), NiPC(24) 112.6(2), PC(11)C(12) 116.4(4), PC(11)C(18) 118.7(4), C(12)C(11)C(18) 118.7(5); NiC(11)PC(24) 108.9(2), NiPC(11)C(18) 113.7(5), NiPC(11)C(12) -94.3(4).

for the three aryl substituents; it is minimal for C(12). Apparently, in addition to electronic factors, other factors also play a role. Inspection of the molecule suggests that the orientation of the aryl rings and attendant steric effects may be important; the *E*-phenyl ring is perpendicular to the ligand plane, which reduces interactions with the bipyridyl system and consequently the pressure on back-bonding. Surprisingly, the sum of bond angles at C(11) (353.8°) is larger than that of the phosphaalkene carbon atom in I (343.5°) [8].

Reflecting the large measure of π-back donation in IV, both phosphorus (δ −16.1 ppm) and carbon (δ 70.6 ppm) exhibit a strong upfield coordination shift relative to II ($\Delta\delta(^{31}P)$ −248.6 ppm; $\Delta\delta(^{13}C)$ −123 ppm [10]). However, there is not a simple direct correlation between coordination shifts and degree of π-back donation, since for I $\Delta\delta(^{31}P)$ was found to be as large as −380 ppm. Both the chemical shifts and the non-equivalence of the β-protons of the bipyridyl moiety prove that η^2-coordination also occurs in solution; the phosphaalkene ligand does not rotate around the σ-bond axis of the η^2-complex on the NMR time scale. However, hindered rotation of the xylyl moiety was observed. Coalescence of ^{1}H signals occurred at 61°C for the *ortho*-methyl groups and at 50°C for the *meta*-ring protons; both temperatures lead to the same $\Delta G^{\neq}$ value of 15.7 ± 0.3 kcal mol^{-1}.

In contrast, interaction between III and Ni(CO)$_4$ led to η^1-coordination. To a solution of III (ca. 0.7 mmol) in $CDCl_3$ Ni(CO)$_4$ (ca. 1 mmol) was added. The ^{31}P NMR spectrum, measured in a sealed tube in order to prevent escape

of carbon monoxide, revealed a ^{31}P signal at δ 211.3 ppm, the typical low-field position for a η^1-coordinated phosphaalkene. We assign this signal to the 1/1 complex VI (eq. 3); in the ^{13}C NMR spectrum, its carbonyl carbons were found at δ 194.0 ppm, the P=C carbon atom at δ 181.6 ppm (^1J(PC) 24 Hz).



(3)

When the reaction between III and $Ni(CO)_4$ was performed without the precautions mentioned above an additional η^1-complex appeared (δ(^{31}P) 216.4 ppm; δ(^{13}C) 195 ppm: CO) to which, by analogy with literature precedent [11], we assign structure VII (eq. 3). These assignments were confirmed by the typical absorptions in the carbonyl region of the IR spectra (CH_2Cl_2): 2076 cm^{-1} (A_1) and 2005 cm^{-1} (E) for VI and 1975 cm^{-1} (B_1) for VII. Both compounds were too unstable to be isolated in pure form, but the η^1-coordination mode is clearly indicated by the spectral data.

In conclusion, our results not only extend the range of η^2-coordination of phosphaalkenes but also demonstrate the influence of the co-ligands on the coordination mode and on the relative importance of σ- and π-bonding.

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10 IV: ^1H NMR (THF-d_8; 25°C; 250 MHz): δ 2.29 (bs, 3H, CH_3); 2.92 (bs, 3H, CH_3); 6.43 ppm (bd, ^3J(HH) 6 Hz, 1H, Xy-*meta*); 6.63—6.74 (m, 4H, Ph); 6.80 (bd, ^3J(HH) 6 Hz, 1H, Xy-*meta*); 6.92 (m, 1H, Xy-*para*); 7.01 (t, ^3J(HH) 7 Hz, 2H, Ph), 7.28—7.39 (m, 3H, 2 Ph + *cis*-Py-*meta*); 7.80 (dd, *J* 8 Hz, *J* 3 Hz, 2H, Ph—*ortho*); 7.94 (m, 4H, Py); 8.66 (d, ^3J(HH) 5 Hz, 1H, N—C—H-*cis*); 9.54 (dd, ^3J(HH) 6 Hz, ^4J(PH) 1 Hz, 1H, N—C—H-*trans*). $^{13}C\{^1H\}$ NMR (THF-d_8; 60°C; 62.90 MHz): δ 26.2 (s, CH_3); 70.6 (d, ^1J(PC) 79 Hz, P=*C*); 121.7—136.7 (m, aryl *CH*); 145.6 (d, ^1J(PC) 52 Hz, P—*C*); 149.8 (d, ^2J(PC) 24 Hz, P=C—*C*, *E*), 151.1 (d, ^2J(PC) 6 Hz, *C*—CH_3); 151.5 (s); 153.0 (d, ^2J(PC) 7 Hz, *C*—CH_3); 155.2 ppm (d, ^2J(PC) 13 Hz, P=C—*C*, *Z*). ^{31}P NMR (THF-d_8; 60°C; 101.26 MHz): δ −16.1.
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