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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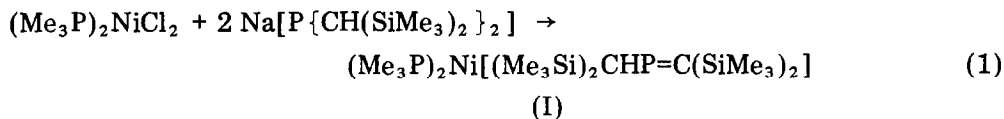
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Summary

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$_2$.
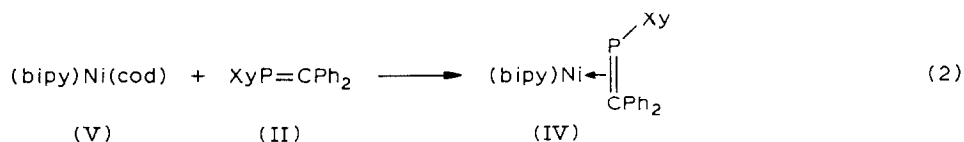

One of the fascinating aspects of the novel phosphaalkenes [1] is their coordination chemistry. Calculations [2,3] and chemical experience [3] indicate that the phosphorus lone pair σ-orbital and the π-orbital of the P=C bond are the highest occupied molecular orbitals of nearly equal energy, and the 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).

$$(Me_3P)_2NiCl_2 \ + \ 2\,Na[P\{CH(SiMe_3)_2\}_2] \ \rightarrow$$

$$(Me_3P)_2Ni[(Me_3Si)_2CHP{=}C(SiMe_3)_2] \qquad (1)$$

$$(I)$$

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).

$$(bipy)Ni(cod) \ + \ XyP{=}CPh_2 \ \longrightarrow \ (bipy)Ni{\leftarrow}\|{\overset{\displaystyle P{\diagup}^{Xy}}{\underset{\displaystyle CPh_2}{}}} \qquad (2)$$

$$(V) \qquad\qquad (II) \qquad\qquad\qquad (IV)$$

(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(diphenyl-methylene)phosphine (III) [3]; in (CO)$_5$Cr·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 nickela-phosphacyclopropane 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
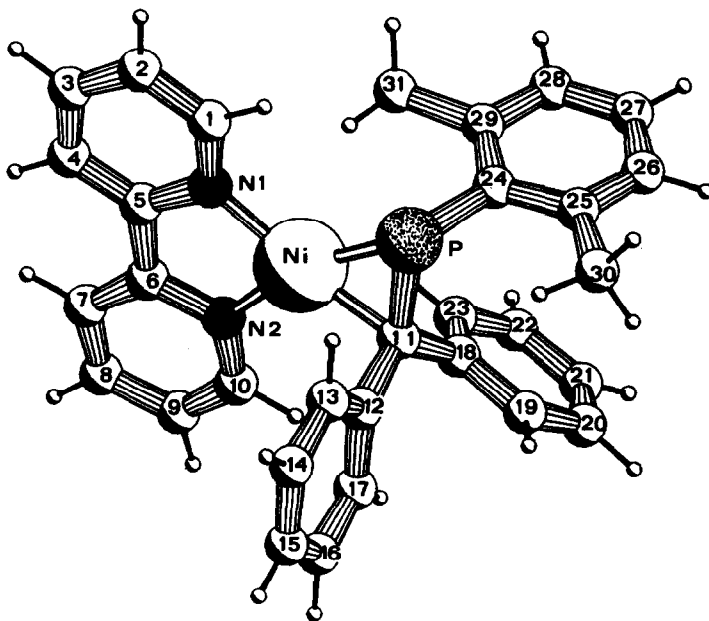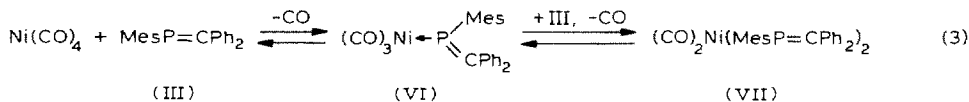

Fig. 1. PLUTO III drawing of (bipy)Ni(XyP=CPh$_2$) (IV), including the adopted numbering scheme. Selected bond lengths (Å), bond angles (°) and torsion angles (°) are: NiP 2.177(2), NiC(11) 1.987(6), NiN(1) 1.940(5), NiN(2) 1.951(5), PC(11) 1.832(6), PC(24) 1.845(6), C(11)C(12) 1.488(8), C(11)C(18) 1.491(8); 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).

$$Ni(CO)_4 + MesP=CPh_2 \underset{-CO}{\overset{-CO}{\rightleftharpoons}} (CO)_3Ni\leftarrow P\overset{Mes}{\underset{CPh_2}{\diagdown}} \underset{+III, -CO}{\rightleftharpoons} (CO)_2Ni(MesP=CPh_2)_2 \qquad (3)$$

$$(III) \qquad\qquad (VI) \qquad\qquad (VII)$$

When the reaction between III and $Ni(CO)_4$ was performed without the precautions mentioned above an additional η^1-complex appeared ($\delta(^{31}P)$ 216.4 ppm; $\delta(^{13}C)$ 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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