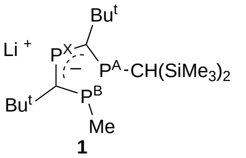
Remarkable 'edge' ligation of a triphosphacyclopentenyl ring system. Synthesis, crystal and molecular structure of $[Ni(\eta^5\text{-}P_3C_2Bu^t{}_2)\{\eta^2\text{-}P_3C_2Bu^t{}_2CH(SiMe_3)_2Me\}]$

Vinicius Caliman, Peter B. Hitchcock and John F. Nixon*

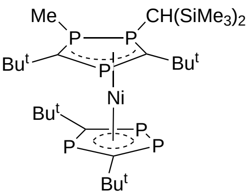
School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ

In the nickel(II) complex $[Ni(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^2\text{-}P_3C_2Bu^t{}_2CH(SiMe_3)_2Me\}]$ the triphosphacyclopentenyl ring $P_3C_2Bu^t{}_2CH(SiMe_3)_2Me$ is unexpectedly coordinated to the metal exclusively *via* the two adjacent saturated ring phosphorus atoms, rather than *via* the 2-phosphaallyl fragment.

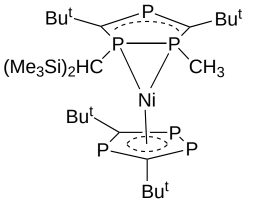
Very recently[1] we reported the synthesis of the lithium triphosphacyclopentenyl salt $LiP_3C_2Bu^t{}_2RR'$ **1** [R = $(Me_3Si)_2CH$, R′ = Me] by treatment of the 1,2,4-triphosphole $P_3C_2Bu^t{}_2R$ **2**[2] with LiMe. The $^{31}P\{^1H\}$ NMR spectrum of **1** can be readily interpreted[1] in terms of the η^3-2-phosphaallylic structure [Fig. 1(*a*)]. Although several ligation modes of the triphosphacyclopentenyl ring anion in **1** towards transition metals can be envisaged, it was anticipated that η^3-ligation *via* the 2-phosphaallyl fragment would be most likely in complexes of nickel(II) halides, however, unexpectedly a completely different type of ligation of the ring to the metal centre occurs as discussed below.



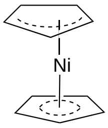
1



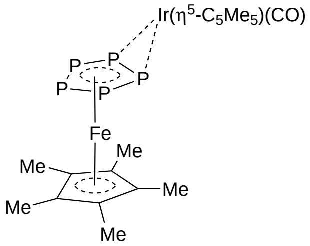
3a



3b



5



6

Treatment of $Li[P_3C_2Bu^t{}_2CH(SiMe_3)_2Me]$ with 1 equiv. of $NiBr_2$ in diethyl ether at −78 °C affords a dark green solution which on further treatment with 1 equiv. of $Li[P_3C_2Bu^t{}_2]$ affords the purple complex $[Ni(\eta^5\text{-}P_3C_2Bu^t{}_2)\{P_3C_2Bu^t{}_2CH(SiMe_3)_2Me\}]$ **3**. Scheme 1 shows the likely steps of the synthesis of **3** *via* the postulated intermediate complex **4** which could not be isolated on account of its air- and moisture-sensitivity. Complex **3** was obtained in 45% yield after chromatography and was fully characterised by mass spectrometry, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.† Its structure, which was confirmed by a single-crystal X-ray diffraction study,‡ surprisingly proved not to involve the expected $\eta^5:\eta^3$ ligation of the two five-membered ring systems which is well known for the related cyclopentadienyl cyclopentenyl nickel(II) complex $[Ni(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)]$ **5**.

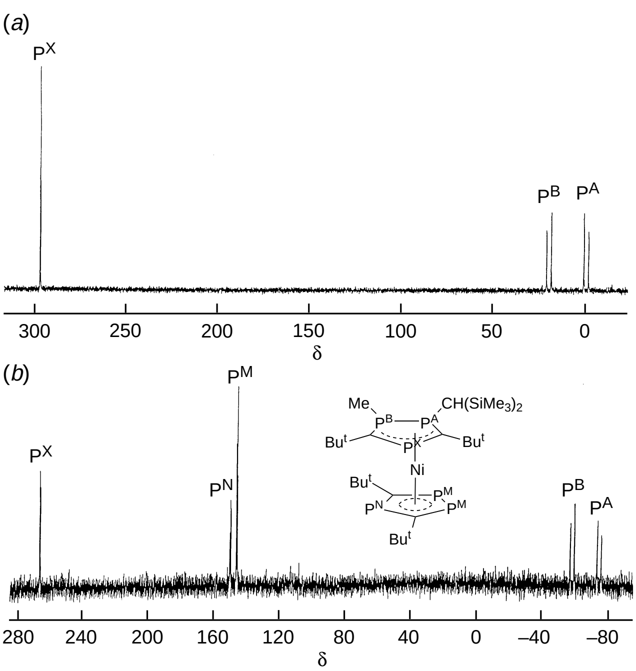
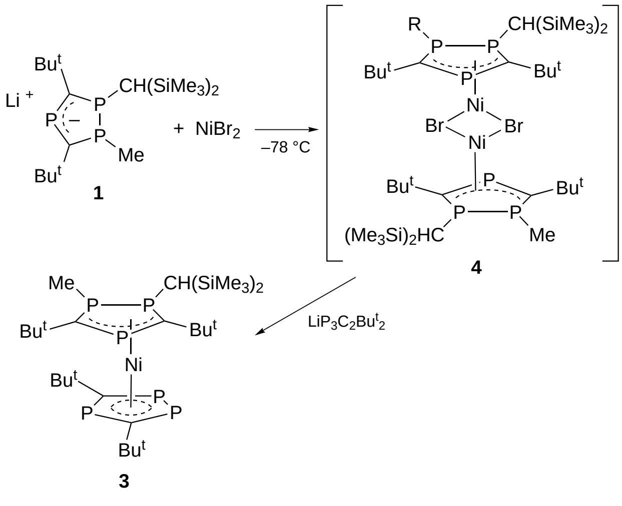


Fig. 1 $^{31}P\{^1H\}$ NMR spectra of (*a*) **1** and (*b*) **3**



Scheme 1

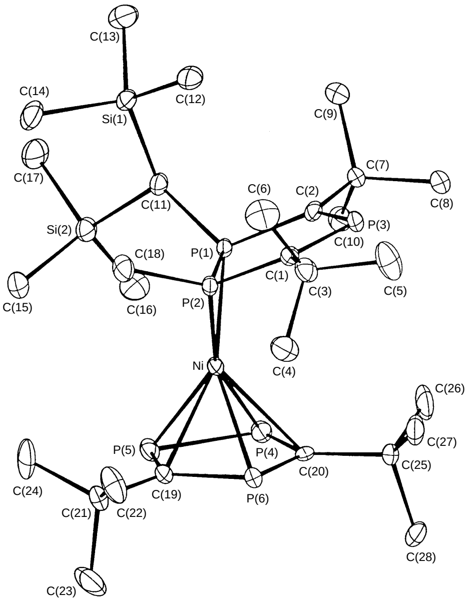


Fig. 2 Molecular structure of **3** with atomic numbering scheme

The $^{31}P\{^1H\}$ NMR spectrum of **3** [Fig. 1(*b*)] exhibits a pattern of lines expected for an [ABM_2NX] spin system. The η^5-$P_3C_2Bu^t_2$ ring gives rise to signals corresponding to P^M and P^N (δ 145.8 and 149.7, respectively) with the expected magnitude of the $^2J_{PP}$ coupling constant for this type of aromatic ring system.[3–6] The pattern of lines observed for the $P_3C_2Bu^t_2CH(SiMe_3)_2Me$ ring in **3** is similar to that exhibited for the free anion in **1**; the P^A and P^B resonances of the two sp^3-hydridised phosphorus showing characteristic high-field resonances (δ P^A -74.5; δ P^B -58.3) with a typically large one bond $^1J_{P^AP^B}$ coupling constants (251.3 Hz), whereas P^X exhibits a typical chemical shift for an sp^2-hybridised phosphorus (δ P^X 266.2), suggesting structure **3a**.

A single-crystal X-ray diffraction study on **3** unexpectedly revealed the remarkable molecular structure **3b** (Fig. 2), in which the 2-phosphaallylic fragment of the $P_3C_2Bu^t_2CH(SiMe_3)_2Me$ ring is not involved in bonding to the nickel, which is in fact solely ligated *via* the P(1) and P(2) lone pair electrons of the two saturated phosphorus centres. The two rings in **3** are both planar, with a dihedral angle of 18°, and structural data are summarised in Fig. 3. The η^5-ligated $P_3C_2Bu^t_2$ ring exhibits bond lengths and angles very similar to several related transition-metal complexes containing this triphospholyl anion.[3–6] The triphosphacyclopentenyl ring $P_3C_2Bu^t_2CH(SiMe_3)_2Me$ in **3** is attached to the Ni^{II} *via* two P–Ni single bonds [P(1)–Ni 2.201(2), P(2)–Ni 2.155(2) Å] and the P(1)–Ni–P(2) bond angle is 58.64(5)°. The intracyclic bond lengths in the triphosphacyclopentenyl ring clearly confirm the partial double bond character expected for the two P–C bonds of the uncoordinated 2-phosphaallylic system [P(3)–C(1) 1.728(5), P(3)–C(2) 1.723(5) Å].

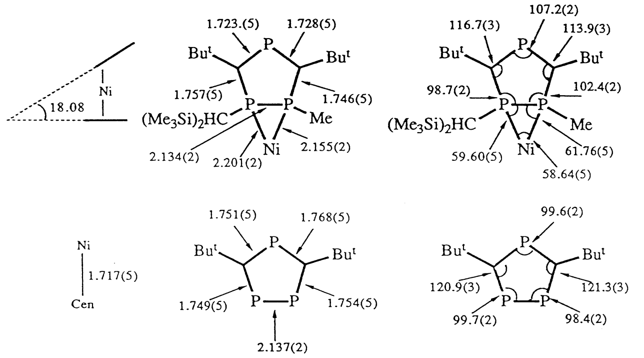


Fig. 3 Important structural features from **3a**. Distances in (Å) and angles in (°).

To our knowledge, the bonding exhibited by the triphosphacyclopentenyl ring in **3** is unprecedented. Scherer and coworkers[7] recently reported the synthesis and molecular structure of the complex [(η^5-C_5Me_5)Fe(μ-$\eta^5:\eta^2$-P_5)Ir(η^5-C_5Me_5)(CO)] **6**, in which there is a η^2-'edge' coordination of the 16-electron [Ir(CO)(η^5-C_5Me_5)] fragment to two adjacent phosphorus atoms in the pentaphospholyl ring. However, the η^2-coordination of the P_5 ring in **6** is completely different to that described for complex **3** above, since it involves an unsaturated P–P ring linkage. It is therefore 'alkene-like' in its ligating mode towards the Ir^I centre, whereas in **3** the two saturated sp^3-hybridised phosphorus atoms must presumably utilise their lone pair electrons in bonding to Ni^{II}. These bonding differences are clearly reflected in the very different P–P bond lengths observed within the η^5-$P_5:\eta^2$-P_5 and η^2-$P_3C_2Bu^t_2CH(SiMe_3)_2Me$ rings in **3** and **6**. There is a significant lengthening (*ca.* 0.2 Å) of the P–P distance in **6** [P(1)–P(2) 2.359(2) Å], compared with that of the parent complex [Fe(η^5-C_5Me_5)(η^5-P_5)],[7] whereas no such elongation results on η^2-coordination of the $P_3C_2Bu^t_2CH(SiMe_3)_2Me$ ring in **3**, and a normal P(1)–P(2) single bond distances [2.134(2) Å] is observed.

We thank CNPq (Brazil) for a studentship (for V. C.) and EPSRC for their continuing support for phosphaalkyne chemistry at Sussex.

Footnotes and References

* E-mail: j.nixon@sussex.ac.uk

† Complex **3**. Satisfactory elemental analyses were obtained. $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6, 25 °C): δ 266.2 (dd, P^X, $^2J_{P^XP^A}$ 33.8, $^2J_{P^XP^B}$ 42.2 Hz), 149.7 (dd P^N, $^2J_{P^NP^M}$ 48.4, $^2J_{P^NP^A}$ 7.2 Hz), 145.8 (dt, P^M, $^2J_{P^MP^N}$ 48.4, $^2J_{P^MP^B}$ 9.2 Hz), -58.3 (ddd, P^B, $^1J_{P^BP^X}$ 251.3, $^2J_{P^BP^M}$ 42.2, $^2J_{P^BP^M}$ 9.2 Hz), -74.5 (ddd, P^A, $^1J_{P^AP^B}$ 251.3, $^2J_{P^AP^X}$ 33.8, $^2J_{P^AP^N}$ 7.2 Hz). ^1H NMR (250.2 MHz, $CDCl_3$, 25 °C): δ -0.16 [s, 9 H, $Si(CH_3)_3$], 0.44 [s, 9 H, $Si(CH_3)_3$], 0.83 (dt, 3 H, PCH_3, $^2J_{HP}$ 6.55, $^3J_{HP}$ 1.37 Hz), 1.10 [s, 9 H, $C(CH_3)_3$], 1.50 [d, 9 H, $C(CH_3)_3$, $^4J_{HP}$ 1.63 Hz], 1.52 [d, 9 H, $C(CH_3)_3$, $^4J_{HP}$ 1.48 Hz], 1.55 [s, 9 H, $C(CH_3)_3$], 2.02 (dd, 1 H, CH, $^2J_{HP}$ 10.54, $^3J_{HP}$ 5.65 Hz). Mass spectrum (EI) for **3**: *m/z*: 694 [$Ni(P_3C_2Bu^t_2)\{P_3C_2Bu^t_2CH(SiMe_3)_2Me\}]^+$ (22%), 535 [$Ni(P_3C_2Bu^t_2)(P_3C_2Bu^t_2Me)]^+$, 405 [$P_3C_2Bu^t_2)(P_3C_2Bu^t_2)]^+$, 73 [$SiMe_3]^+$.

‡ *Crystal data* for **3**: $C_{28}H_{58}NiP_6Si_2$, M = 695.45, monoclinic, space group $P2_1/c$ (no. 14), a = 10.782(3), b = 19.243(4), c = 19.319(7) Å, β = 94.75(2)°, U = 3995(2) Å^3, Z = 4, D_c = 1.16 g cm^{-3}, $F(000)$ = 1488. Monochromated Mo-Kα radiation λ = 0.710 69 Å, T = 173(2) K. Data were collected on an Enraf-Nonius CAD 4 diffractometer using a crystal of 0.40 × 0.40 × 0.20 mm. A total of 7010 unique reflections were measured for $2 < \theta < 25°$ of which 5120 had $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS-86 and refined on F^2 with all non-H atoms anisotropic using SHELXL-93. H atoms were included in riding mode with U_{iso} = 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl groups. The final residuals were R_1 = 0.058 [for $I > 2\sigma(I)$] and wR_2 = 0.158 for all data. CCDC 182/553.

1 V. Caliman, P. B. Hitchcock, J. F. Nixon and N. Sakarya, *Bull. Soc. Chim. Belg.*, 1996, **105**, 675.
2 V. Caliman, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1995, 1661.
3 R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 1146.
4 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327 and references therein.
5 J. F. Nixon, *Chem. Soc. Rev.*, 1995, 319 and references therein.
6 J. F. Nixon, *Coord. Chem. Rev.*, 1995, **145**, 201 and references therein.
7 M. Detzel, G. Friedrich, O. J. Scherer and G. Wolmershausen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1321.

Received in Cambridge, UK, 2nd June 1997; 7/03797J