Preliminary communication

Phospholyl compounds of nickel and uranium

Thérèse Arliguie, Michel Ephritikhine *, Monique Lance, Martine Nierlich

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA Saclay, 91191 Gif sur Yvette, France

Abstract

The phospholyl nickel compound $[\{Ni(\eta^5\text{-}C_4Me_4P)(\mu\text{-}\eta^1\text{-}C_4Me_4P)\}_2]$ **1** was prepared by treating $NiCl_2$ with two equivalents of KC_4Me_4P in pyridine, whereas reaction of $NiCl_2$ with two equivalents of $[U(\eta^5\text{-}C_4Me_4P)_3Cl]$ or an excess of $[U(\eta^5\text{-}C_4Me_4P)_2Cl_2]$ afforded the trinuclear complex $[Ni\{(\mu\text{-}\eta^5,\eta^1\text{-}C_4Me_4P)_2UCl_2\}_2]$ **2**. Reduction of a 1:2 mixture of **1** and $[U(\eta^5\text{-}C_4Me_4P)_2Cl_2]$ by sodium amalgam in tetrahydrofuran gave the tetranuclear compound $[\{Ni_2(\mu\text{-}\eta^1\text{-}C_4Me_4P)_2\}\{(\mu\text{-}\eta^5,\eta^1\text{-}C_4Me_4P)_2UCl_2\}_2 \cdot 3C_4H_8O]$ **3**. The crystal structures of **1**, **2** and **3** have been determined.

Keywords: Phospholyl; Nickel; Uranium

1. Introduction

A remarkable aspect of the phospholyl (phosphacyclopentadienyl) ligand is its ability to bridge two metal centres through the available lone pair on the phosphorus atom [1] and we thought to take advantage of this feature for building polynuclear compounds in which d transition metals and f elements would be associated. By using the tetramethylphospholyl group as the bridging ligand, we synthesized the first complexes with uranium and nickel atoms in close proximity. Furthermore, as no η^5-phospholyl derivative of nickel had been so far reported, we were also interested in isolating the first example in this class.

2. Results and discussion

The reaction of $NiCl_2$ with two equivalents of KC_4Me_4P [2] in pyridine led to the formation of compound **1**, $[(\eta^5\text{-}C_4Me_4P)Ni(\mu\text{-}\eta^1\text{-}C_4Me_4P)_2Ni(\eta^5\text{-}C_4Me_4P)]$, which was isolated as a bright red microcrystalline powder, stable in air.

Crystal data for **1**: crystal dimensions 0.55 × 0.30 × 0.25 mm, monoclinic, space group $C2/c$, $a = 21.659(5)$, $b = 8.729(2)$, $c = 22.042(5)$ Å, $\beta = 125.08(2)°$, $V = 3411(2)$ Å^3, $Z = 4$, $\rho_{calcd} =$

1.313 g cm^{-3}, $2 < 2\theta < 40°$, $\omega\text{-}2\theta$ scan mode, $\mu(\text{Mo K}\alpha) = 13.13$ cm^{-1}, $F(000) = 1424$, $T = 295$ K. 1866 reflections collected, 1649 unique, 1151 reflections with $I > 3\sigma(I)$. Data were corrected for Lorentz-polarization effects and decay (loss of 3% in 19 h, linearly corrected). The structure was solved by direct method (SHELXS-86) and refined by full-matrix least squares (F) with anisotropic thermal parameters for Ni and P atoms; H atoms were not introduced. The final R value was 0.072 ($R_w = 0.099$, $w = 1$). Difference Fourier analysis showed no peaks beyond +0.81 or −0.64 e Å^{-3}. Diffraction data were recorded on an Enraf–Nonius CAD4 diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). All calculations were performed on a Vax 4000-200 computer with the Enraf–Nonius MolEN system. Further details on the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

The centrosymmetric crystal structure of **1** (Fig. 1) consists of discrete dimeric molecules in which two $Ni(\eta^5\text{-}C_4Me_4P)$ fragments are linked by two phospholyl ligands which are bridging in a μ^2-P fashion. The geometrical parameters of the NiP1Ni^{i}P1^i lozenge are quite identical to those determined in the nickel(II) complex $[\{Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}PPh_2)\}_2]$ [3] (Table 1). In this latter compound, the C_5H_5 ring was suspected to be slightly distorted, as it could also be observed in other cyclopentadienyl complexes [5]; in the absence of
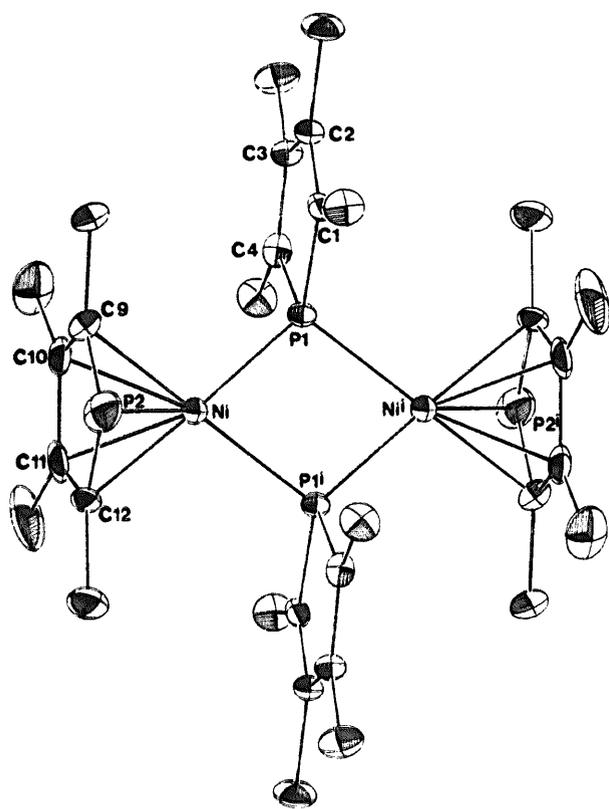
---

* Corresponding author.

Fig. 1. Crystal structure of 1. Symmetry code: (i) 1 − x, − y, 1 − z. Displacement ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and angles (deg): P1−C1 1.79(1), P1−C4 1.80(1), C1−C2 1.32(2), C2−C3 1.47(2), C3−C4 1.35(2), Ni−P2 2.335(5), Ni−C(η-C₄Me₄P) 2.11(2), P2−C9 1.67(1), P2−C12 1.79(2), C9−C10 1.37(2), C10−C11 1.46(2), C11−C12 1.41(2); P1−C1−C2 110(1), P1−C4−C3 110(1), C1−P1−C4 91.2(6), C1−C2−C3 116(1), C2−C3−C4 113(1), P2−C9−C10 116(1), P2−C12−C11 114(1), C9−P2−C12 89.0(8), C9−C10−C11 114(1), C10−C11−C12 107(1). See also Table 1.

intermolecular packing forces, this phenomenon was explained theoretically by symmetry arguments which predict a localization of electron density in the cyclopentadienyl ligand [6]. In compound 1, the distortion of the planar η⁵-phospholyl ring is more obvious. In particular, the P2−C9 bond distance (1.67(1) Å) is much shorter than P2−C12 (1.79(2) Å) while the C9−C10−C11 and C10−C11−C12 angles are also significantly different (114(1) and 107(1)°); these P−C bond distances and endocyclic C−C−C angles are typically equal

to 1.77 Å and 113° in the other η⁵-phospholyl complexes of the d transition metals and f elements [1]. The metal−C(η⁵-phospholyl) bond lengths are equal within experimental error with a value of 2.11(2) Å which may be compared with those found in the phosphacymantrene [Mn{η⁵-C₄Me₂H(COPh)P}(CO)₃] [7] (2.17 Å), the phosphaferrocenes [Fe(η⁵-C₄Me₂H₂P)₂] [8] (2.06 Å) and [Fe(η⁵-C₄Me₂H₂P)(η⁵-C₅H₅)] [9] (2.05 Å) and the triple-decker compound [(η⁵-C₄Me₄P)Co(Et₂C₂B₃H₃)Co(η⁵-C₄Me₄N)] [10] (2.08 Å). The geometry of the bridging phospholyl ligand is regular with a normal C1=C2−C3=C4 unit and equal P1C1 and P1C4 bond distances. The solid state structure of 1 is retained in solution, as shown by the ¹H and ³¹P NMR spectra which exhibit the signals corresponding to the two distinct phospholyl ligands: ¹H NMR (C₅D₅N, 20°C, 200 MHz, TMS int.). δ = 2.13 (t, J = 6 Hz, 12 H, α-Me of μ-C₄Me₄P), 1.67 and 1.48 (s, 12 H + 12 H, β-Me), 0.90 (d of t, J = 10 and 3 Hz, α-Me of η-C₄Me₄P); ³¹P {H} NMR (C₅D₅N, 20°C, 81 MHz, 85% H₃PO₄ ext.). δ = 11.3 (t, J = 3.5 Hz, 2 P, η-C₄Me₄P), −11?.8 (t, J = 3.5 Hz, 2 P, μ-C₄Me₄P); the upfield ³¹P resonance is characteristic of phosphido-bridged compounds with no metal−metal bonding [11].

With the aim of preparing novel U−Ni complexes, we considered some reactions of NiCl₂ with uranium phospholyl derivatives. Treatment of NiCl₂ with one equivalent of [U(η⁵-C₄Me₄P)₂Cl₂] or [U(η⁵-C₄Me₄P)₃Cl] [12] afforded the dinuclear compound 1 which was separated from the not identified uranium side-products by crystallization. Such ligand exchange reactions are classical in actinide chemistry [13].

In a further experiment, a pyridine solution of NiCl₂ and [U(η⁵-C₄Me₄P)₃Cl] in the molar ratio of 1:2 was heated for 5 h at 110°C and deposited dark red, air sensitive, rod-like microcrystals. The X-ray diffraction study revealed the trinuclear structure of compound 2, [Cl₂U(μ-η⁵,η¹-C₄Me₄P)₂Ni(μ-η⁵,η¹-C₄Me₄P)₂UCl₂]. (Fig. 2). Crystal data for 2: crystal dimensions 0.35 × 0.20 × 0.15 mm, triclinic, space group P1̄, a = 13.99(1), b = 16.91(2), c = 17.627(7) Å, α = 80.11(5), β = 87.04(4), γ = 74.38(7)°, V = 3957(11) Å³, Z = 4, ρcalcd = 2.070 g cm⁻³, 2 < 2θ < 40°, ω−2θ scan mode, μ(Mo Kα) = 86.708 cm⁻¹,

Table 1
Geometry of the NiPNiP lozenge in μ-phosphido nickel compounds

Compound	Ni−Ni (Å)	Ni−P (Å)	Ni−P−Ni (deg)	P−Ni−P (deg)
[{Ni(η⁵-C₅H₅)(μ-PPh₂)}₂] [3]	3.36(1)	2.15(1)	102.4(3)	77.6(5)
1	3.340(3)	2.17(1)	100.7(1)	79.3(1)
[{Ni(μ-PPh₂)(CO)₂}₂] [4]	2.510(5)	2.193(2)	69.8(3)	110.1(3)
3	2.546(9)	2.202(7)	70.6(3)	109.4(3)

$F(000) = 2320$, $T = 295$ K. 7871 reflections collected, 7362 unique, 4650 reflections with $I > 3\sigma(I)$, empirical absorption correction (max. and min. transmission factors 0.436, 0.999). Data were corrected for Lorentz-polarization effects and decay (loss of 10% in 82 h, linearly corrected). The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares (F) with anisotropic thermal parameters for all non-C atoms; H atoms were not introduced. The refinement converged at $R = 0.045$ and $R_w = 0.055$ ($w = 1$). Difference Fourier analysis showed no peaks beyond $+0.84$ or $-0.66 e \text{Å}^{-3}$. Diffraction data were recorded on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073 \text{Å}$). All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MolEN system. Further details on the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.) The unit cell contains two independent and quite identical molecules in which the central nickel atom is chelated by two U(μ-η^5,η^1-C$_4$Me$_4$P)$_2$Cl$_2$ metalloligands; the pseudo S_4 U-Ni-U axis deviates from linearity by 2 and 5°. The nickel-phosphorus bond lengths average 2.18(2) Å and lie in the range of Ni-P bond distances in tetrakis(organophosphane) nickel complexes which vary from 2.13 to 2.21 Å [14-24]. The P-Ni-P angles range from 105.3(3) to 114.7(3)°, indicating that the tetrahedral coordination geometry of the Ni atom is not much distorted, compared with the rare structures of NiP$_4$ frameworks with monophosphane ligands [14-16] ; more severe distor-

tions are usually encountered in chelate complexes of the type Ni(P-P)$_2$ [16-24]. The U-Ni distances which average 3.38(2) Å are not favourable for a strong interaction between the two metal centres [25]; among the other trinuclear compounds which exhibit such an [M](μ-P)$_2$ Ni(μ-P)$_2$[M'] system (μ-P = bridging phosphorous ligand), [{Zr(η^5-C$_5$H$_5$)$_2$(μ-CH$_2$PMe$_2$)$_2$}$_2$ Ni] [22], [{Cr(μ-η^6,η^1-C$_6$H$_5$PMe$_2$)$_2$}$_2$ Ni] [23] and [Zr(η^5-C$_5$H$_5$)$_2$(μ-PEt$_2$)$_2$Ni(μ-PEt$_2$)$_2$Hf(η^5-C$_5$H$_5$)] [24], it is only in this latter that a three centre [Zr] $\cdot \cdot$ Ni $\cdot \cdot$ [Hf] bonding orbital has been considered. The tetrahedral coordination around uranium is not different from that invariably found in the monomeric complexes [M(η^5-phospholyl)$_2$X$_2$] (and [M(η^5-cyclopentadienyl)$_2$X$_2$]) [12,26]; it has already been noted that this geometry is most favourable for the formation of chelate derivatives [1]. Complex 2 was prepared in a more rational way by treating NiCl$_2$ with [U(η^5-C$_4$Me$_4$P)$_2$Cl$_2$] and Na(Hg) (two equivalents each) or with an excess of [U(η^5-C$_4$Me$_4$P)$_2$Cl$_2$]; such syntheses of Ni(PR$_3$)$_4$ compounds by reduction of a nickel(II) complex in the presence or with an excess of PR$_3$ are well documented [27]. Complex 2 was characterized by its NMR spectra. ^{1}H NMR (C$_5$D$_5$N, 20°C, 200 MHz, TMS int.) : $\delta = 49.2$ and -30.8 (s, 24H + 24H); ^{31}P{H} NMR (C$_5$D$_5$N, 20°C, 81 MHz, 85% H$_3$PO$_4$ ext.) $\delta = 199.2$ (s).

The reaction of NiCl$_2$ with two equivalents of [U(η^5-C$_4$Me$_4$P)$_2$Cl] was carried out at room temperature in tetrahydrofuran and it was surprising to find that the crystals which were formed after 10 h had exactly the same aspect as 2 but were in fact a co-precipitate of 2 and another new derivative 3, [Cl$_2$U(μ-η^5,η^1-
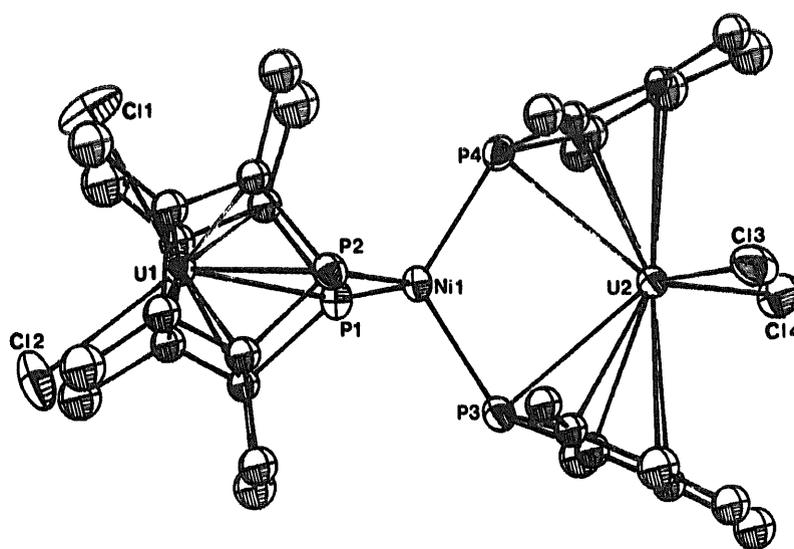

Fig. 2. Crystal structure of one of the two independent molecules of 2. Displacement ellipsoids are shown at the 40% probability level. Carbon atoms labels have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1-P1 2.191(8), Ni1-P2 2.161(8), Ni1-P3 2.199(8), Ni1-P4 2.188(8), U1-P1 2.860(7), U1-P2 2.823(7), U2-P3 2.855(7), U2-P4 2.862(7), ⟨U-C(η-C$_4$Me$_4$P)⟩ 2.86(5), ⟨U-Cl⟩ 2.58(1), Ni1-U1 3.381(3), Ni1-U2 3.365(3); P1-Ni1-P2 113.0(3), P1-Ni1-P3 107.9(3), P1-Ni1-P4 109.6(3), P2-Ni1-P3 105.7(3), P2-Ni1-P4 106.0(3), P3-Ni1-P4 114.7(3), Cl1-U1-Cl2 97.7(3), Cl3-U2-Cl4 100.2(3), centroid(C$_4$Me$_4$P1)-U1-centroid(C$_4$Me$_4$P2) 142.7(8), centroid(C$_4$Me$_4$P3)-U2-centroid(C$_4$Me$_4$P4) 143.8(8).

$C_4Me_4P)_2Ni(\mu-\eta^1-C_4Me_4P)_2Ni(\mu-\eta^5,\eta^1-C_4Me_4P)_2-UCl_2 \cdot 3C_4H_8O]$. The trinuclear compound **2** was not obtained by further reduction or heating of **3**, suggesting that this latter was not an intermediate in the formation of **2** but was the product of an independent and concomitant reaction. Single crystals of **3** were isolated after reduction of a 1:2 mixture of **1** and $[U(\eta^5-C_4Me_4P)_2Cl_2]$ by means of sodium amalgam. Crystal data for **3**: crystal dimensions $0.40 \times 0.30 \times 0.25$ mm, orthorhombic, space group *Pnnm*, $a = 12.134(4)$, $b = 20.021(10)$, $c = 14.660(5)$ Å, $V = 3562(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.666$ g cm^{-3}, $2 < 2\theta < 40°$, $\omega-2\theta$ scan mode, μ(Mo Kα) = 51.443 cm^{-1}, $F(000) = 1756$, $T = 295$ K. 1998 reflections collected, 1745 unique, 989 reflections with $I > 3\sigma(I)$, empirical absorption correction (max. and min. transmission factors 0.788, 0.999). Data were corrected for Lorentz-polarization effects and decay (loss of 10% in 22 h, linearly corrected). The structure was solved by direct method (SHELXS-86) and refined by full-matrix least squares (F) with anisotropic thermal parameters for all non-O and -C atoms. Three disordered solvent molecules were found in the last difference-Fourier. H atoms were not introduced. The final R value was 0.054 ($R_w = 0.065$, $w = 1$). Difference Fourier analysis showed no peaks beyond $+0.92$ or -0.97 e Å^{-3}. All calculations were performed on a Vax 4000-200 computer with the Enraf–Nonius MolEN system. Further details on the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The tetranuclear structure of **3** (Fig. 3) appears to be derived from that of **1** by replacing each η^5-phospholyl group by two phosphorus atoms of a $U(\mu-\eta^5,\eta^1-C_4Me_4P)_2Cl_2$ metalloligand; the molecular symmetry is C_{2h}. If the geometry of the

$U(C_4Me_4P)_2Cl_2$ fragment is similar to that observed in **2**, the structural parameters of the Ni_2P_2 array are quite different from those determined in **1**, owing to the formation of the Ni–Ni bond which permits each metal atom to achieve its 18e ground state configuration; the NiP3Ni^{ii}P3^i lozenge is then identical to that found in the dimeric nickel(I) compound $[\{Ni(\mu-PPh_2)(CO)_2\}_2]$ [4] (Table 1). The ^{1}H and ^{31}P NMR spectra of **3** exhibited very broad resonances and were not interpretable.

If it seems likely that compounds **2** and **3** result respectively from the reduction of $NiCl_2$ and **1** in the presence of $[U(\eta^5-C_4Me_4P)_2Cl_2]$, the mechanism of their formation from $NiCl_2$ and $[U(\eta^5-C_4Me_4P)_3Cl]$ is still unclear; the nature of the reducing species and of the side-products have to be determined. However, the synthesis of **2** and **3**, and also that of **1**, bring out the high versatility of the phospholyl ligand which, by adopting various coordination modes in the same assembly, favours the building of homo- and heteropolynuclear compounds.

3. Experimental section

1. A solution of $NiCl_2$ (155 mg, 1.20 mmol) and KC_4Me_4P (427 mg, 2.40 mmol) in pyridine (50 ml) was heated for 10 h at 100 °C. The solvent was evaporated off and the residue was extracted in a Soxhlet apparatus with tetrahydrofuran (50 ml). The red microcrystalline powder of **1** obtained after evaporation was washed with tetrahydrofuran and dried under vacuum (370 mg, 92%). Correct elemental analyses (C, H, P).

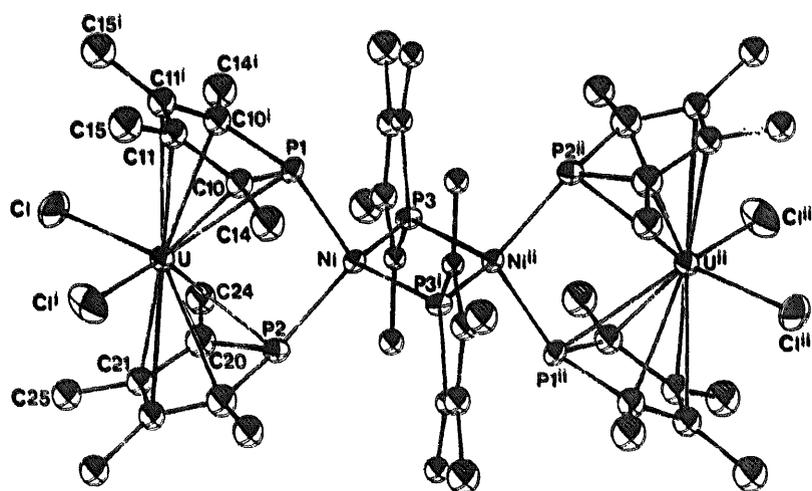2. (a) A mixture of $NiCl_2$ (20.5 mg, 0.16 mmol) and $[U(\eta^5-C_4Me_4P)_3Cl]$ (218.4 mg, 0.32 mmol) in pyridine

Fig. 3. Crystal structure of **3** (the compound is a solvate with three molecules of tetrahydrofuran). Symmetry code: (i) x, y, $-z$, (ii) $-x$, $1 - y$, $-z$, (iii) $-x$, $1 - y$, z; P1, P2, U and Ni atoms are located in the mirror plane and P3 on the diad axis. Displacement ellipsoids are shown at the 40% probability level; some carbon atoms labels have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–P1 2.17(1), Ni–P2 2.16(1), U–P1 2.86(1), U–P2 2.851(9), U–Cl 2.587(8), Ni–U 3.513(5); P1–Ni–P2 108.7(4), P1–Ni–P3 109.1(2), P2–Ni–P3 110.2(2), Cl–UCl^i 99.6(5), centroid(C$_4$Me$_4$P1)–U–centroid(C$_4$Me$_4$P2) 138.7(5). See also Table 1.

(30 ml) was stirred for 5 h at 100 °C. The hot solution was filtered and upon cooling deposited dark red microcrystals of **2**; these were filtered off, washed with pyridine and dried under vacuum (84 mg, 43%). Correct elemental analyses (C, H, P). (b) An NMR tube, charged with $NiCl_2$ (1.4 mg, 0.011 mmol) and $[U(\eta^5\text{-}C_4Me_4P)_2Cl_2]$ (25.3 mg, 0.043 mmol) in pyridine (1 ml) was smoothly shaken for 24 h at 20 °C. The red crystals of **2** were decanted off, washed with tetrahydrofuran and dried under vacuum (2.1 mg, 16%).

3. A mixture of **1** (118 mg, 0.175 mmol), $[U(\eta^5\text{-}C_4Me_4P)_2Cl_2]$ (205.6 mg, 0.35 mmol) and 2% Na(Hg) (403 mg, 0.35 mmol of Na) in tetrahydrofuran (50 ml) was stirred for 10 h at 20 °C. Red microcrystals of **3** (approximate yield 20%) were formed but could not be cleanly separated from NaCl and other unidentified products.

References

[1] H.J. Gosink, F. Nief, L. Ricard and F. Mathey, *Inorg. Chem.*, *34* (1995) 1306; F. Mathey, *Coord. Chem. Rev.*, *137* (1994) 1; L. Brunet, F. Mercier, L. Ricard and F. Mathey, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 742; P. Gradoz, M. Ephritikhine, M. Lance, J. Vigner and M. Nierlich, *J. Organomet. Chem.*, *481* (1994) 69; D.A. Atwood, A.H. Cowley and S.M. Dennis, *Inorg. Chem.*, *32* (1993) 1527; F. Nief, F. Mathey and L. Ricard, *J. Organomet. Chem.*, *384* (1990) 271; R.M.G. Roberts, J. Silver and A.S. Wells, *Inorg. Chim. Acta*, *119* (1986) 165; B. Deschamps, F. Mathey, J. Fischer and J.H. Nelson, *Inorg. Chem.*, *23* (1984) 3455; J. Fischer, A. Mitschler, L. Ricard and F. Mathey, *J. Chem. Soc. Dalton Trans.*, (1980) 2522; G. de Lauzon, B. Deschamps and F. Mathey, *New J. Chem.*, *4* (1980) 683; F. Mathey, *J. Organomet. Chem.*, *154* (1978) C13.

[2] P. Gradoz, D. Baudry, M. Ephritikhine, F. Nief and F. Mathey, *J. Chem. Soc. Dalton Trans.*, (1992) 3047.

[3] J.M. Coleman and L.F. Dahl, *J. Am. Chem. Soc.*, *89* (1967) 542.

[4] J.A.J. Jarvis, R.H.B. Mais, P.G. Owston and D.T. Thompson, *J. Chem. Soc. A:*, (1970) 1867.

[5] P.L. Holland, R.A. Andersen and R.G. Bergman, *J. Am. Chem. Soc.*, *118* (1996) 1092; A.E. Smith, *Inorg. Chem.*, *11* (1972) 165; M.J. Bennett, M.R. Churchill, M. Gerloch and R. Mason, *Nature*, *201* (1964) 1318.

[6] L.F. Dahl and C.H. Wei, *Inorg. Chem.*, *2* (1963) 713.

[7] F. Mathey, A. Mitschler and R. Weiss, *J. Am. Chem. Soc.*, *100* (1978) 5748.

[8] G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem. Soc.*, *102* (1980) 994.

[9] F. Mathey, A. Mitschler and R. Weiss, *J. Am. Chem. Soc.*, *99* (1977) 3537.

[10] K.J. Chase, R.F. Bryan, M.K. Woode and R.N. Grimes, *Organometallics*, *10* (1991) 2631.

[11] P.E. Garrou, *Chem. Rev.*, *81* (1981) 229; P.E. Kreter and D.W. Meek, *Inorg. Chem.*, *22* (1983) 319.

[12] P. Gradoz, D. Baudry, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, *J. Organomet. Chem.*, *466* (1994) 107; P. Gradoz, C. Boisson, D. Baudry, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc. Chem. Commun.*, (1992) 1720.

[13] J.C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc. Dalton Trans.*, (1995) 3019.

[14] W.S. Sheldrick, *Acta Crystallogr. Sect. B:*, *31* (1975) 305.

[15] M.B. Hursthouse, K.J. Izod, M. Motevalli and P. Thornton, *Polyhedron*, *13* (1994) 151.

[16] C. Elschenbroich, M. Nowotny, A. Behrendt, W. Massa and S. Wocadlo, *Angew. Chem. Int. Ed. Engl.*, *31* (1992) 1343.

[17] P. Le Floch, L. Ricard, F. Mathey, A. Jutand and C. Amatore, *Inorg. Chem.*, *34* (1995) 11.

[18] C. Krüger and Y.H. Tsay, *Acta Crystallogr. Sect. B:*, *28* (1972) 1941.

[19] H. Brunner, G. Vitulli, W. Porzio and M. Zocchi, *Inorg. Chim. Acta*, *96* (1985) 67.

[20] H. Hartung, U. Baumeister, B. Walther and M. Maschmeier, *Z. Anorg. Allg. Chem.*, *578* (1989) 177.

[21] G. Müller and H.H. Karsch, *Acta Crystallogr. Sect. C:*, *43* (1987) 663.

[22] H.H. Karsch, G. Müller and C. Krüger, *J. Organomet. Chem.*, *273* (1984) 195.

[23] C. Elschenbroich, G. Heikenfeld, M. Wünsch, W. Massa and G. Baum, *Angew. Chem. Int. Ed. Engl.*, *27* (1988) 414.

[24] R.T. Baker, W.C. Fultz, T.B. Marder and I.D. Williams, *Organometallics*, *9* (1990) 2357.

[25] J.V. Ortiz, *J. Am. Chem. Soc.*, *108* (1986) 550; J.M. Ritchey, A.J. Zozulin, D.A. Wrobleski, R.R. Ryan, H.J. Wasserman, D.C. Moody and R.T. Paine, *J. Am. Chem. Soc.*, *107* (1985) 501.

[26] D. Baudry, M. Ephritikhine, F. Nief, L. Ricard and F. Mathey, *Angew. Chem. Int. Ed. Engl.*, *29* (1990) 1485.

[27] C.A. McAuliffe and W. Levason, *Phosphine, Arsine and Sulphine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1979, p. 169.