Unusual Alkylidene-bridged Complexes of Nickel by α-H Abstraction from a Nickelacycle. Crystal and Molecular Structure of [{$Ni_2(CHCMe_2$-*o*-$C_6H_4)Cl(PMe_3)_2$}$_2$]

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The pseudoallylic complex [Ni(η^3-$CH_2C_6H_4$-*o*-Me)Cl(PMe_3)] effects α-H abstraction from the metallacycle [$Ni(CH_2CMe_2$-*o*-$C_6H_4)(PMe_3)_2$] under very mild conditions, with formation of an alkylidene-bridged tetrametallic species of composition [{$Ni_2(CHCMe_2$-*o*-$C_6H_4)Cl(PMe_3)_2$}$_2$].

We have recently reported that the benzannelated nickelacycle [$Ni(CH_2CMe_2$-*o*-$C_6H_4)(PMe_3)_2$] **1** can be readily obtained[1] by δ-H abstraction from the unstable dialkyl [$Ni(CH_2CMe_2Ph)_2(PMe_3)_2$]. We now report that, under appropriate conditions, **1** can undergo an α-H abstraction which yields a compound of composition [{$Ni_2(CHCMe_2$-*o*-C_6H_4)-$Cl(PMe_3)_2$}$_2$] **2** that contains one alkylidene bridging ligand[2–5] per Ni_2 unit. This transformation provides the first reported example of α-elimination from a metallacycle to give an isolable alkylidene complex.[6] Moreover, compound **2** is to our knowledge the first non-heteroatom-stabilized alkylidene complex of nickel. Mononuclear, heteroatom-stabilized alkylidene complexes of Ni are known[2,7] but analogous homo- and hetero-binuclear derivatives are rare.[8] The formation of the transient Cp(L)Ni=CH_2^+ (Cp = C_5H_5; L = P-donor ligand) has been postulated in some methylene transfer reactions[9] and a methylene-bridged W–Ni complex has been characterized recently.[10]

Treatment of a yellow–orange solution of **1** with the pseudoallylic species[11] [Ni(η^3-$CH_2C_6H_4$-*o*-Me)Cl(PMe_3)]

yields dark-red, almost black crystals of **2**. Full spectroscopic data† for this compound are available, and its molecular structure has been determined by X-ray studies.‡ The molecular complex **2** (Fig. 1) has a centre of symmetry which relates the two binuclear units that comprise the planar, six-membered Ni_4Cl_2 ring. The chlorine atoms bridge the non-bonded pairs of Ni atoms whereas the alkylidene and aryl ligands symmetrically bridge the two bonded pairs of Ni atoms. The Ni–Ni separation, within these binuclear units [2.384(3) Å], is close to the 2.32–2.36 Å range typical of Ni–Ni bonds in sterically favoured situations.[12] The existence of a single Ni–Ni bond[13,14] can also be invoked to explain the observed diamagnetism of compound **2**.

The overall formation of **2** from the dialkyl $[Ni(CH_2CMe_2Ph)_2(PMe_3)_2]$ corresponds to a double H-abstraction, $\delta + \alpha$. In accord with the stoichiometry proposed in Scheme 1, the best yields of **2** (80% of isolated product) are obtained when the starting materials are mixed in a 1:2 molar ratio. Therefore, in addition to capturing the leaving PMe_3 ligand, the pseudoallyl complex acts as an H-acceptor (yielding *o*-dimethylbenzene, GC–MS) and provides a suitable metal fragment, allowing the formation of the observed dimetallacyclopropane structure.[5a,15] This synthetic methodology can be successfully applied to the preparation of other related alkylidene complexes of nickel. Thus, treatment of the metallacycle **1** with the 18 e complex $[(\eta^5\text{-}C_5H_5)Ni(\eta^3\text{-}C_3H_5)]$ provides good yields of the binuclear, alkylidene-bridged complex **3** (Scheme 2), which has been fully characterized by spectroscopic† and X-ray studies (to be reported separately).

The dimeric nature of the tetrametallic complex **2** suggests that related binuclear alkylidene compounds could be isolated by rupture of the chloride bridges (Scheme 3). Treatment of **2** with 1 equiv. of PMe_3 produces the rather unstable complex **4** while in the presence of an excess of PMe_3, $[Ni(PMe_3)_4]$ and the ylide†[16] complex **5** are obtained. This transformation is highly reminiscent of the reported reaction of PMe_3 with the heteronuclear μ-methylene complex $[Cp_2Ta(CH_3)(\mu\text{-}CH_2)Pt(PMe_3)_2]$, which gives[17] $[Pt(PMe_3)_4]$ and the terminal methylene compound $[Cp_2Ta(CH_2)CH_3]$, and may proceed *via* formation of an unstable mononuclear alkylidene species, $[Ni(CHCMe_2\text{-}o\text{-}C_6H_4)Cl(PMe_3)]$, followed by nucleophilic

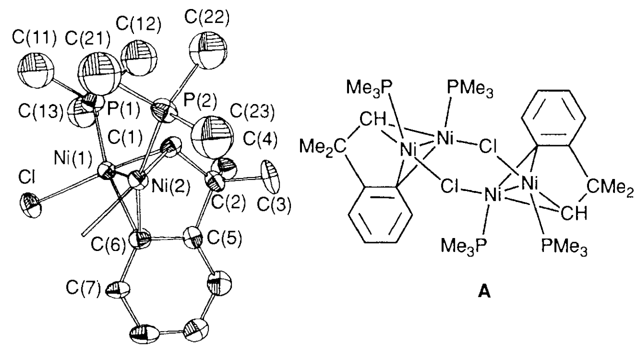
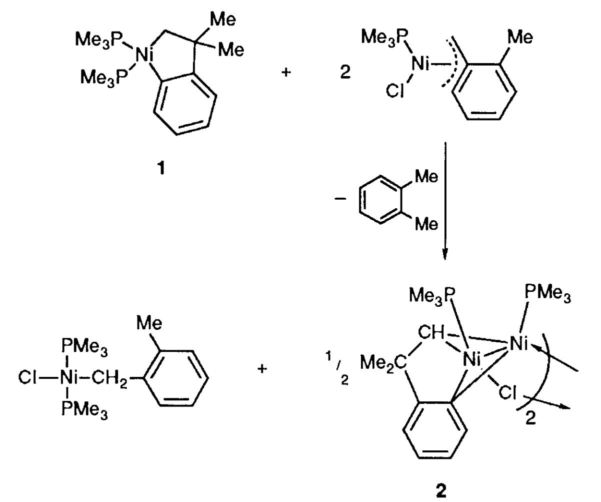
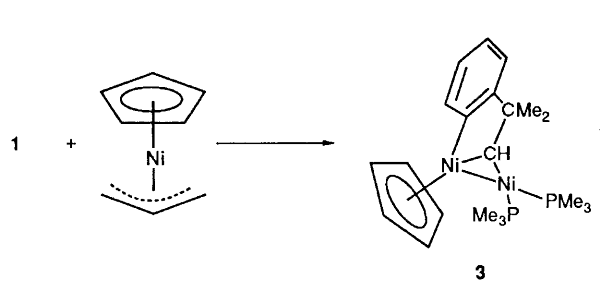


Fig. 1 ORTEP diagram for **2** and schematic representation **A**, with atom labelling scheme. Only half of the molecule is represented for clarity and all methyl groups and H atoms have been omitted. Important bond distances (Å) and angles (°): Ni(1)–Ni(2) 2.384(3), Ni(1)–C(1) 1.91(2), Ni(1)–C(2) 2.306(6), Ni(1)–P(1) 2.180(6), Ni(1)–C(6) 2.04(2); C(1)–Ni(1)–C(6) 75.8(8), Ni(1)–C(1)–Ni(2) 77.6(7), Ni(1)–C(6)–Ni(2) 71.2(7), P(1)–Ni(1)–C(1) 94.7(6), C(1)–Ni(2)–P(2) 95.8(6).



Scheme 1



Scheme 2 C_6H_6, 40 °C, $-C_3H_6$

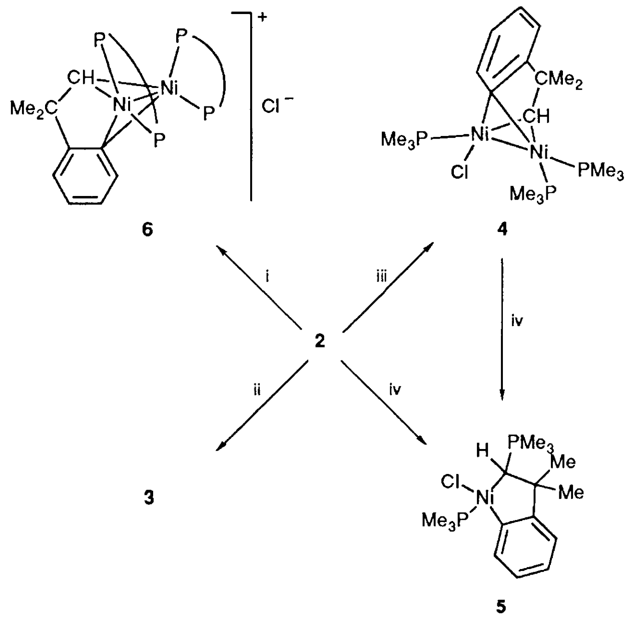
† *Selected spectroscopic data* for **2**: ^1H NMR (CD_3CN) δ 1.35 (d, $^2J_{HP}$ 8.3 Hz, 18H, 2 PMe_3), 1.41 (s, 6H, 2 Me) and 3.45 (t, $^3J_{HP}$ 14.3 Hz, 1H, Ni_2CH); $^{31}P\{^1H\}$ NMR (CD_3CN) δ −9.2 s; $^{13}C\{^1H\}$ NMR (CD_3CN) δ 15.1 (d, $^1J_{CP}$ 26 Hz, PMe_3), 34.9 (s, CMe_2), 57.2 (s, CMe_2) and 120.2 (br s, Ni_2CH). Satisfactory elemental analyses were obtained for $C_{32}H_{58}Cl_2P_4Ni_4\cdot 1/3C_6H_6$.

Complex **3**: ^1H NMR (C_6D_6) δ 0.74 (d, $^2J_{HP}$ 5.9 Hz, 9H, PMe_3), 0.83 (d, $^2J_{HP}$ 7.3 Hz, 9H, PMe_3), 1.49, 1.65 (s, 3H and 3H, CMe_2), 5.5 (s, 5H, C_5H_5) and 7.02 (dd, $^3J_{HP}$ 6.6 and 2.3 Hz, 1H, Ni_2CH); $^{31}P\{^1H\}$ NMR (C_6D_6), δ −23.9 (d, $^2J_{PP}$ 32 Hz) and −17.7 (d); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 16.9 (d, $^1J_{CP}$ 19.1 Hz, PMe_3), 18.7 (dd, $^1J_{CP}$ 22 Hz, $^3J_{CP}$ 5 Hz, PMe_3), 30.4 (dd, $^4J_{CP}$ 8 and 3 Hz, CMe), 36.9 (d, $^4J_{CP}$ 9 Hz, CMe), 59.8 (s, CMe_2), 90.2 (s, C_5H_5) and 161.4 (d, $^2J_{CP}$ 43 Hz, Ni_2CH).

Complex **5**: ^1H NMR (CD_3COCD_3) δ 1.24 (d, $^2J_{HP}$ 7.8 Hz, 9H, Ni-PMe_3), 1.47 (d, $^2J_{HP}$ 13.1 Hz, 9H, $CHPMe_3$) and 1.99 (dd, J_{HP} 6.2 and 5.3 Hz, 1H, $CHPMe_3$); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ −12.7 (d, J_{AX} 10.1 Hz, Ni-P_A) and 21.8 (d, CHP_X); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 14.5 (d, $^1J_{CP}$ 54 Hz, $CHPMe_3$), 14.9 (d, $^1J_{CP}$ 22 Hz, Ni-PMe_3) and 43.3 (dd, $^2J_{CP}$ 68 Hz, $^1J_{CP}$ 27 Hz, $CHPMe_3$).

Complex **6**: ^1H NMR (CD_2Cl_2) δ 4.61 (tt, $^3J_{HP}$ 14.4 and 1.5 Hz, 1H, Ni_2CH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.6 (d, J_{AX} 7.4 Hz, P_A) and 35.0 (d, P_X); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 126.9 (t, $^2J_{CP}$ 8 Hz, Ni_2CH).

‡ *Crystal data* for **2**: $C_{32}H_{58}Cl_2Ni_4P_4$, M_r = 872.44, monoclinic, space group $P2_1/n$, a = 9.815(4), b = 10.550(4), c = 19.669(7) Å, β = 104.39(3)°, V = 1973(1) Å^3, Z = 4, D_c = 1.47 g cm^{-3}, $F(000)$ = 912, μ(Mo-Kα) = 22.08 cm^{-1}. The crystals were dark red, prismatic and polysynthetically twinned on (100) with b and c in common. One of these crystals (0.4 × 0.2 × 0.2 mm) was coated with epoxy resin and mounted in a Kappa diffractometer. The cell dimensions were refined by least squares fitting the values of 25 reflections. The intensities [4356 collected; 1767 'observed,' with $I > 2\sigma(I)$] were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion correction for Ni, Cl and P were taken from the International Tables. The structure was solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinement. The refinement involved anisotropic thermal parameters for the non-hydrogen atoms with the exception of the PMe_3 carbon atoms, which showed a non-resolved disorder and were refined isotropically. The hydrogen atoms were included with fixed contributions at their calculated positions. Final R = 8.8%; R_w = 10.0%. The maximum residual electronic density was 2 e Å^{-3} around the methyl groups. Most of the calculations were carried out with the X-Ray 80 system.[19] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 3 *Reagents*: i, dmpe; ii, $Na(C_5H_5)$; iii, PMe_3 (1 equiv.); iv, PMe_3 (excess)

attack of a PMe_3 ligand at the carbene carbon. On the other hand, action of the chelating phosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) on **2** (Scheme 3) affords† the cationic, symmetrically bridged, alkylidene complex **6**.[18] Finally, the reaction of **2** with NaCp provides an alternative synthesis of **3**.

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