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COMMUNICATION

X-RAY CRYSTAL STRUCTURE OF [Ni{η^2-C(NBu^t)CH(SiMe$_3$)$_2$}Cl(PMe$_3$)], THE FIRST STRUCTURALLY CHARACTERIZED η^2-ALKANEIMIDOYL COMPLEX OF NICKEL

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Abstract—The alkylation of [NiCl$_2$(PMe$_3$)$_2$] with Mg[CH(SiMe$_3$)$_2$]Cl yielded the alkyl dimer [Ni{CH(SiMe$_3$)$_2$}(μ-Cl)(PMe$_3$)]$_2$ (1), which readily inserted CNBu^t to afford [Ni{η^2-C(NBu^t)CH(SiMe$_3$)$_2$}Cl(PMe$_3$)] (4); spectroscopic and X-ray studies reveal this complex contains an η^2-alkaneimidoyl ligand.

The migratory insertion of carbon monoxide and organic isocyanides into transition metal–carbon bonds are reactions of fundamental importance in organometallic chemistry.[1] With some exceptions,[2] η^2-acyl or η^2-iminoacyl (alkaneimidoyl) structures are characteristics of compounds of the early transition metals, the lanthanides and the actinides.[1,3,4] Later transition elements give predominantly η^1 formulations, although η^2-alkaneimidoyl complexes of Fe, Ru and Co are known[5] and bridging η^2-alkaneimidoyl linkages have also been demonstrated[6,7] for some late elements.

We have recently shown that the existence of bulky environments favours the formation of η^2-alkaneimidoyl complexes of nickel.[8] Although these species were characterized by spectroscopic techniques, single crystals could not be obtained for any of the compounds prepared thus preventing their structural characterization by X-ray methods. Using a similar approach, now based on the use of the bulky bis(trimethylsilyl)methyl alkyl group, CH(SiMe$_3$)$_2$, we have carried out the first X-ray structural characterization of an η^2-alkaneimidoyl complex of nickel, [Ni{η^2-C(NBu^t)CH(SiMe$_3$)$_2$}Cl(PMe$_3$)] (4). Attempts to prepare an analogous η^2-acyl derivative have proved unsuccessful.

The slow reaction of the chloride complex [NiCl$_2$(PMe$_3$)$_2$] with stoicheiometric amounts of the Grignard reagent Mg[CH(SiMe$_3$)$_2$]Cl occurred with loss of PMe$_3$ and formation[†] of the alkyl derivative [Ni{CH(SiMe$_3$)$_2$}(μ-Cl)(PMe$_3$)]$_2$ (1) (Scheme 1).

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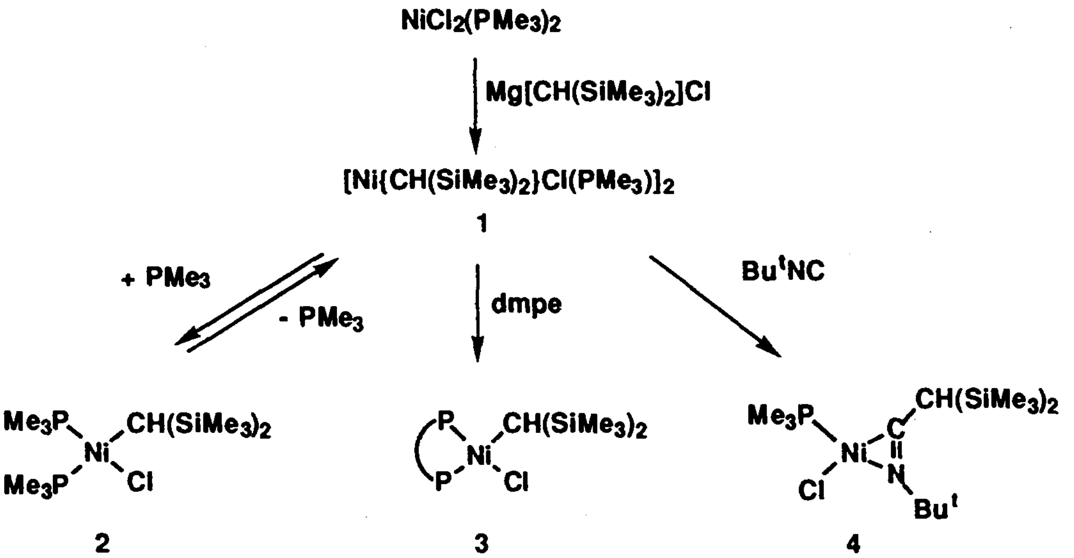
[†] To a cold (-50°C) suspension of [NiCl$_2$(PMe$_3$)$_2$] (3.00 g, 10.6 mmol) in Et$_2$O (100 cm^2), Mg[CH(SiMe$_3$)$_2$]Cl was added (16.6 cm^3 of a solution 0.64 M in Et$_2$O, *ca* 10.6 mmol) and the resulting mixture stirred for 2 h at this temperature and for a further 16 h at room temperature. After removal of the volatiles *in vacuo*, extraction with three portions of petroleum ether (45 cm^3) and cooling at -20°C, compound **1** was obtained as red–violet crystals in 65% yield (2.25 g). Mol. wt. (cryoscopically in C$_6$H$_6$, N$_2$) Found: 679. Calc. for C$_{20}$H$_{56}$Cl$_2$Ni$_2$P$_2$Si$_4$: 659. Found: C, 36.3; H, 8.6. Calc. for C$_{20}$H$_{56}$Cl$_2$Ni$_2$P$_2$Si$_4$: C, 36.4; H, 8.6%. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ -1.40 [d, 1 H, ^3J(H—P) 17.2 Hz, Ni—CH], 0.60 [s, 18 H, (SiMe$_3$)$_2$], 0.72 [d, 9 H, ^2J(H—P) 9.7 Hz, PMe$_3$]. ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ -15.6 s. ^{13}C-{^{1}H} NMR (C$_6$D$_6$) δ -5.8 [d, ^2J(C—P) 24 Hz, Ni—CH], 4.7 [s, (SiMe$_3$)$_2$], 14.4 [d, ^1J(C—P) 32 Hz, PMe$_3$].



Scheme 1.

Analytical and molecular weight (cryoscopically in benzene) determinations are in accord with the proposed dimeric formulation.[9] Since related alkyl compounds *trans*-$[Ni(R)Cl(PMe_3)_2]$[10] ($R = CH_2SiMe_3$, CH_2CMe_2Ph) show no tendency to lose one of the PMe_3 ligands and undergo concomitant dimerization, the formation of **1** by the reaction route depicted in Scheme 1 is very likely directed by the steric requirements of the alkyl group.

Addition of an excess of PMe_3 (3–4 equivalents) to solutions of **1** gave the expected alkyl monomer *cis*-$[Ni\{CH(SiMe_3)_2\}Cl(PMe_3)_2]$ (**2**).*

The rather unusual *cis* geometry of this complex seems to be a consequence of the steric bulkiness of the alkyl group. Compound **2** loses PMe_3 slowly in solution, although it is sufficiently stable at room temperature for full spectroscopic characterization. A related compound, *cis*-$[Ni\{CH(SiMe_3)_2\}Cl(dmpe)]$ (**3**) ($dmpe = Me_2PCH_2CH_2PMe_2$) can be obtained by reaction of **1** with the diphosphine ligand. Not unexpectedly, the chelating nature of dmpe provides enhanced stability of **3**, as compared to **2**.

To fulfil the main goals of this work, namely the isolation of η^2-acyl and η^2-iminoacyl complexes of nickel, the reactions of **1** with carbon monoxide and $CNBu^t$ were investigated. Most unfortunately, the reaction of **1** (or **2**) with carbon monoxide did not give an isolable acyl, even when effected by low temperatures (*ca* $-50°C$) and employing stoicheiometric amounts of carbon monoxide. Instead it provided the known carbonyl cluster $Ni_4(CO)_6(PMe_3)_4$,[11] together with some other unidentified products. The reaction of **1** with $CNBu^t$ followed a different course yielding (1 equivalent $CNBu^t$, $-30°C$) an orange crystalline solid of analytical composition† "$Ni[CH(SiMe_3)_2]Cl(CNBu^t)(PMe_3)$", which exists as a monomeric species, both in solution and in the solid state (*vide infra*). The observation of a medium intensity IR absorption at *ca* 1675 cm^{-1} and of a ^{13}C-$\{^1H\}$ NMR resonance

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* Satisfactory analytical and spectroscopic data for all new compounds have been obtained.

† To a solution of compound **1** (0.24 g, 0.36 mmol) in Et_2O (60 cm^3), cooled at $-50°C$, $CNBu^t$ was added (0.7 cm^3 of a *ca* 1 M solution in THF). The mixture was slowly warmed to $-30°C$ and evaporated to dryness at this temperature. The yellow residue was extracted with 30 cm^3 of a 1 : 1 petroleum ether/diethyl ether mixture and after centrifugation, concentration to *ca* 15 cm^3 and cooling to $-30°C$, yellow crystals of **4** (0.27 g, *ca* 0.66 mmol) were isolated in *ca* 90% yield. Recrystallization of this material from Et_2O gave crystals of analytical purity. Mol. wt. (cryoscopically in C_6H_6, N_2) Found: 416. Calc. for $C_{15}H_{37}ClNNiPSi_2$: 413. Found: C, 43.3; H, 8.9; N, 3.3. Calc. for $C_{15}H_{37}ClNNiPSi_2$: C, 43.6; H, 9.0; N, 3.4%. ^1H NMR (200 MHz, C_6D_6) δ 0.04 [s, 18 H, $(SiMe_3)_2$], 1.11 [d, 9 H, $^2J(H—P)$ 8.1 Hz, PMe_3], 1.35 (s, 9 H, CMe_3), 1.67 [s, 1 H, $CH(SiMe_3)_2$]. ^{31}P-$\{^1H\}$ NMR (C_6D_6) δ −9.5 s. ^{13}C-$\{^1H\}$ NMR (CD_3COCD_3) δ 0.74 [s, $(SiMe_3)_2$], 16.1 [d, $^1J(C—P)$ 26 Hz, PMe_3], 23.3 [d, $^3J(C—P)$ 4 Hz, $CH(SiMe_3)_2$], 29.8 (s, CMe_3), 57.3 (s, CMe_3), 163.6 [d, $^2J(C—P)$ 13 Hz, $Ni—C{=}N$].

in the proximity of δ 164 [d, ^2J(C—P) 13 Hz] suggests that this complex contains an η^2-alkaneimidoyl ligand resulting from the insertion of a molecule of CNBu^t into the Ni—C bond of **1**, and it should therefore be formulated as [Ni{η^2-C(NBu^t)CH(SiMe$_3$)$_2$}Cl(PMe$_3$)] (**4**). Although neither the value of ν(C═N) nor the chemical shift of the metal-bound alkaneimidoyl carbon can be used as consistent parameters for the identification of the bonding mode of the alkaneimidoyl ligand,[8] the similarity of the above values with those previously found for related η^2-alkaneimidoyl complexes of nickel[8] supports the dihapto formulation. For example, Ni-η^1-C(NBu^t)R linkages are characterized by ν(C═N) and δ(Ni—C) values of around 1600 cm^{-1} and 185 ppm, respectively,[8] while for Ni-η^2-C(NBu^t)R units corresponding values are of *ca* 1700 cm^{-1} and 170 ppm, respectively.

To confirm the validity of the above spectroscopic assignments and to unequivocally ascertain the bonding mode of the alkaneimidoyl ligand, an X-ray structural determination of **4** has been undertaken. Figure 1 shows an ORTEP[12] perspective view of the molecules of **4** and includes also some relevant bond distances and angles.* If the alkaneimidoyl ligand is considered to occupy a single coordination site [the bite angle C(1)—Ni—N is only of 39.3(6)°] the Ni atom is in a planar three-coordinate environment, consisting of the chloro, phosphine and alkaneimidoyl ligands. The most interesting feature of this structure is doubtless the Ni-η^2-alkaneimidoyl linkage which displays short Ni—C(1) and Ni—N bonding interactions [1.84(1) and 1.82(1) Å, respectively] and also a short C(1)—N bond of 1.23(2) Å, intermediate between a double (1.31 Å) and a triple (1.16 Å) bond. In the recently prepared [(Me$_3$P)$_2$BrNi{μ_2,η^2-C(NXy)CH$_2$-o-C$_6$H$_4$}NiBr(PMe$_3$)] complex (Xy = 2,6-dimethylphenyl), that contains a bridging η^2-alkaneimidoyl ligand,[7] the corresponding distances are (Ni—C) 1.866(9) Å, (Ni—N) 1.977(8) Å and (C—N) 1.312(11) Å, respectively. The relative short C(1)—N bond in **4** compares well with the analogous distance in η^2-imidoyl complexes of the early transition metals, thus showing that short C—N interations are not exclusive to the latter compounds, but it is in contrast with the relatively long C—N bond of 1.301(1) Å found in the ruthenium complex [Ru{C(N-p-tol)p-tol}Cl(CO)(PPh$_3$)$_2$].[5a]

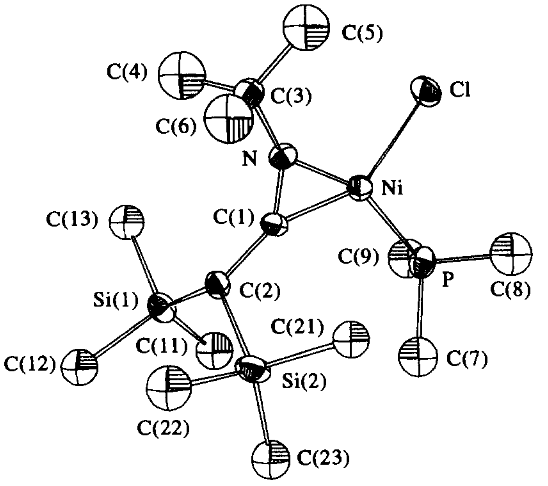

Fig. 1. Molecular structure of **4** and atom labelling scheme. Selected bond distances (Å) and angles (°) include the following: Ni—N = 1.82(1); Ni—C(1) = 1.84(1); Ni—Cl = 2.239(5); Ni—P = 2.153(5); N—C(1) = 1.23(2); N—Ni—C(1) = 39.3(6); P—Ni—C(1) = 117.9(5); N—Ni—Cl = 108.0(4); P—Ni—Cl = 95.0(2).

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* *Crystal data for* **4**: C$_{15}$H$_{37}$ClNNiPSi$_2$, M = 412.7, orthorhombic, $P2_12_12_1$, a = 10.959(2), b = 11.126(5), c = 19.56(1) Å, U = 2385(2) Å^3, Z = 4, D_c = 1.15 g cm^{-3}, λ (Mo-$K\alpha$) = 0.71069 Å (graphite monochromator), μ = 10.9 cm^{-1}, 295 K, Kappa diffractometer, $\omega/2\theta$ scan technique. An orange crystal (0.3 × 0.2 × 0.2 mm) was coated with an epoxy resin and mounted in a Kappa diffractometer. The cell dimensions were refined by least squares, fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Of 4681 reflections measured, 1660 [$I \geq 2\sigma(I)$] were used in the refinement. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, P, Si and Cl were taken from the *International Tables for X-Ray Crystallography*.[13] The structure was solved by Patterson and Fourier methods. An empirical absorption correction[14] was applied at the end of the isotropic refinement. There exists some non-resolvable disorder from the thermal motions of the C atoms of the methyl groups. Consequently these atoms were only refined isotropically. No trend in ΔF *vs* F or sin θ/λ was observed. A final mixed refinement with unit weights and fixed isotropic factors and coordinates for H atoms was undertaken. R = 0.073 and R_w = 0.079. A final difference synthesis showed no significant electron density. Most of the calculations were carried out with the XRAY 80 system.[15] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited as supplementary material.

REFERENCES

1. L. D. Durfee and I. P. Rothwell, *Chem. Rev.* 1988, **88**, 1059; H. Werner, *Angew. Chem., Int. Ed. Engl.* 1990, **29**, 1077.
2. G. Erker, M. Mena, C. Krüger and R. Noe, *Organometallics* 1991, **10**, 1201; R. Fandos, A. Meetsma and J. H. Teuben, *Organometallics* 1991, **10**, 2665; K. Mashima, H. Haraguchi, A. Ohyoshi, N. Sakai and H. Takaya, *Organometallics* 1991, **10**, 2731; Z. Guo, D. S. Swenson, A. S. Guram and R. F. Jordan, *Organometallics* 1994, **13**, 766.
3. V. Skagestad and M. Tilset, *Organometallics* 1992, **11**, 3293, and references cited therein.
4. P. Zanella, G. Paolucci, G. Rosseto, F. Benetollo, A. Polo, R. D. Fischer and G. Bombieri, *J. Chem. Soc., Chem. Commun.* 1985, 96; A. L. Gerrit, J. Vogelzang and J. A. Teuben, *Organometallics* 1992, **11**, 2273; A. Antiñolo, M. Fajardo, R. Gil-Sanz, C. López-Mardomingo, A. Otero, A. Atmani, M. M. Kubicki, S. El Krami, Y. Mugnier and Y. Mourad, *Organometallics* 1994, **13**, 1200.
5. (a) W. R. Roper, G. E. Taylor, J. Waters and L. J. Wright, *J. Organomet. Chem.* 1978, **157**, C27; (b) H. Werner, S. Lotz and B. Heiser, *J. Organomet. Chem.* 1981, **209**, 197; (c) G. Bellachioma, G. Cardaci, A. Macchioni and G. Reichenbach, *Inorg. Chem.* 1992, **31**, 63.
6. R. Usón, J. Forniés, P. Espinet, E. Lalinde, A. García, P. G. Jones, K. Meyer-Bäse and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* 1986, 259; D. Seyferth and J. B. Hoke, *Organometallics* 1988, **7**, 524; R. Bertani, A. Berton, F. Di Bianca and B. Crociani, *J. Organomet. Chem.* 1988, **348**, 411; A. Klose, E. Solari, R. Ferguson, C. Floriani, A Chiesi-Villa and C. Rizzoli, *Organometallics* 1993, **12**, 2414; K.-L. Lu, H.-J. Chen, P.-Y. Lu, S.-Y. Li, F.-E. Hong, S.-M. Peng and G.-H. Lee, *Organometallics* 1994, **13**, 585.
7. J. Cámpora, E. Carmona, E. Gutiérrez. P. Palma, M. L. Poveda and C. Ruiz, *Organometallics* 1992, **11**, 11; J. Cámpora, E. Gutiérrez, A. Monge, M. L. Poveda, C. Ruiz and E. Carmona, *Organometallics* 1993, **12**, 4025.
8. E. Carmona, P. Palma, M. Paneque and M. L. Poveda, *Organometallics* 1990, **9**, 583.
9. H. F. Klein and H. H. Karsch, *Chem. Ber.* 1973, **106**, 1433.
10. E. Carmona, F. González, M. L. Poveda, J. L. Atwood and R. D. Rogers, *J. Chem. Soc., Dalton Trans.* 1980, 2108.
11. M. Bochmann, I. Hawkins, L. J. Yellowlees, M. B. Hursthouse and R. L. Short, *Polyhedron* 1989, **8**, 1351.
12. C. K. Johnson, ORTEP II, Oak Ridge National Laboratory, Tennessee (1971).
13. *International Tables for X-Ray Crystallography*, Vol. 4, pp. 72–98. Kynoch Press, Birmingham (1974).
14. N. Walker and D. Stuart, *Acta Crystallogr., Sect. A* 1983, **39**, 158.
15. J. M. Stewart, XRAY 80 System, Computer Science Center, University of Maryland, College Park, Maryland (1985).