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Mono- and di-nickellaazaphosphiranes of mono- and bis-(amido)cyclodiphosph(III)azanes†

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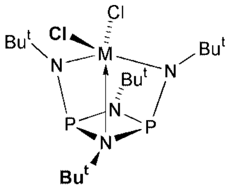
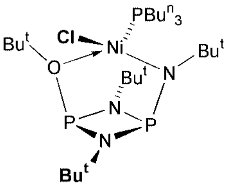
The syntheses and solid-state structures of the first three-membered nickel–phosphorus–nitrogen ring compounds, having anionic four-electron P=N moieties are reported.

Most modern homogeneous catalysts, which polymerize olefins to macromolecules with predictable properties, are mixtures of early-transition metal compounds and Lewis-acidic Group 13 cocatalysts.[1] Recently Brookhart and Gibson demonstrated that similar mixtures of late-transition metal complexes, particularly those with chelating bis(imino) ligands, also polymerize olefins with excellent activities.[2] Even more promising are single-component, late transition-metal alkyls, because they are both active in the absence of the expensive cocatalyst and they polymerize polar olefins.[3] The unusual properties of these neutral compounds and their polymers have rekindled interest in transition metals, especially iron, cobalt and nickel, that were once considered unlikely candidates for polyolefin catalysis.

We previously reported bis(amido)cyclodiphosph(III)azane complexes **A** of group 4 metals, which form polyethylene, but have comparatively short lifetimes.[4] Follow-up studies showed that the Lewis-acidic medium deactivates the catalyst by the ring opening of the cyclodiphosph(III)azane. This caused us to test the suitability of these heterocycles as ligands for neutral late-transition metal catalysts. To synthesize such complexes we modified the cyclodiphosph(III)azane to a monoanionic version, because one chloride ligand is required for polymer-chain growth.



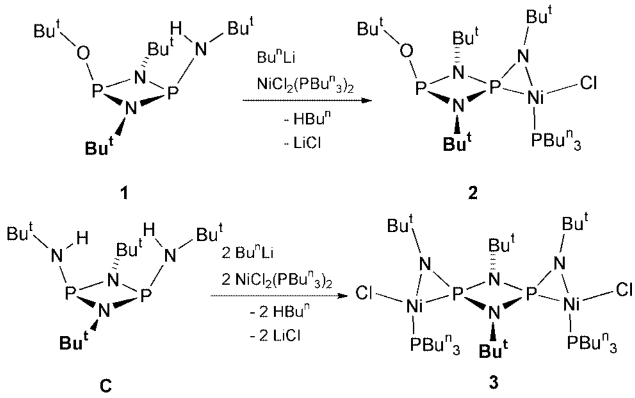
A



B

By treating $NiCl_2(PBu^n_3)_2$ with *cis*-[Bu^{t}OP(μ-NBu^t)$_2$PN-Bu^t]$^-$ (Scheme 1) we hoped to obtain precatalyst **B** and activate it by alkylation. Although both, tetrahedral and planar, coordination geometries were conceivable, the diamagnetism of the orange–red product **2**‡ indicated that the nickel atom was planar or almost planar. The uncommon chemical shift of one of the heterocycle's phosphorus atoms (−53.1 ppm and *ca.* 170 ppm upfield of that of pristine ligand), however, suggested an unusual ligand coordination.

This suspicion was confirmed by an X-ray analysis, Fig. 1, which showed that in **2**§ the amidocyclodiphosph(III)azane is not the expected *N,O*-chelate, but an η^2-*P,N* ligand, instead. Compound **2** is a spirocycle of three- and four-membered rings, whose crystallographic *m* symmetry implies a perfectly-planar nickel environment, although some of the bond angles [*e.g.* P1–Ni–N1 45.62(9)°] are far from ideal square planar. The Ni–Cl [2.2175(10) Å] and Ni–P3 [2.1522(12) Å] bond lengths, however, are quite similar to those in related nickel–chloro–amido–phosphine complexes.[5]



Scheme 1

To test the generality of the reaction we repeated it with the bifunctional bis(amino)cyclodiphosph(III)azane **C** (Scheme 1), for which *N,N* chelation seemed a distinct plausibility. Treatment of $\{NiCl_2[P(Bu^n)_3]_2\}$ with dianionic **C** afforded again a dark-red, diamagnetic complex **3**.‡ The X-ray analysis, Fig. 2,§ confirmed that **3** was an almost C_2-symmetric, dinuclear analogue of **2**, whose nickel atoms exhibited bond parameters that are isometric with each other and those of **2**.

A survey of the bond lengths of **2** and **3** reveals that the amidocyclodiphosph(III)azanes are not simple amido ligands with auxiliary nickel–phosphorus interactions. Thus, the metal-

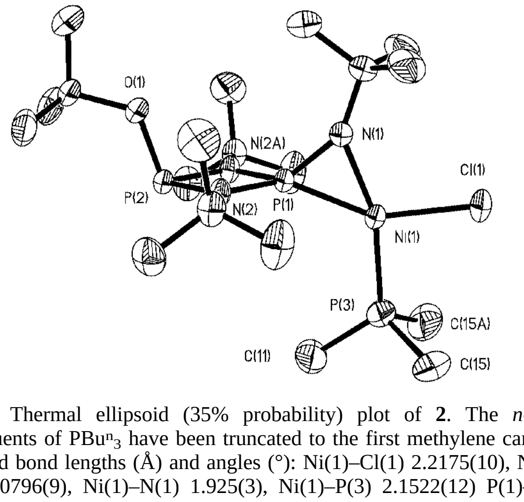


Fig. 1 Thermal ellipsoid (35% probability) plot of **2**. The *n*-butyl substituents of PBu^n_3 have been truncated to the first methylene carbons. Selected bond lengths (Å) and angles (°): Ni(1)–Cl(1) 2.2175(10), Ni(1)–P(1) 2.0796(9), Ni(1)–N(1) 1.925(3), Ni(1)–P(3) 2.1522(12) P(1)–N(1) 1.559(3); P(3)–Ni(1)–Cl(1) 92.95(5), N(1)–Ni(1)–Cl(1) 105.55(9), P(1)–Ni(1)–N(1) 45.62(9), P(1)–Ni(1)–P(3) 115.88(5).

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† Electronic supplementary information (ESI) available: experimental section and crystallography. See http://www.rsc.org/suppdata/cc/b1/b105359k/

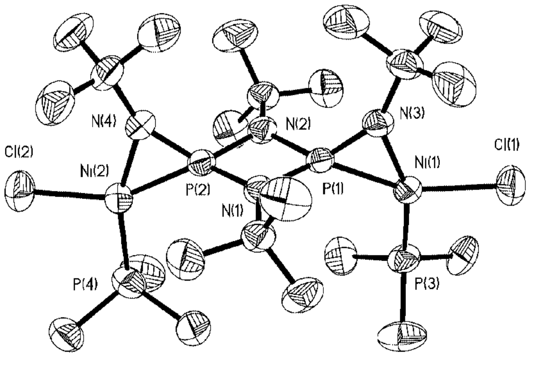
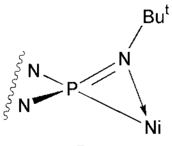
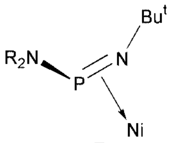


Fig. 2 Thermal ellipsoid (35% probability) plot of **3**. The *n*-butyl substituents of both PBu^n_3 ligands have been truncated to the first methylene carbons. Selected bond lengths (Å) and angles (°): Ni(1)–Cl(1) 2.2001(16), Ni(2)–Cl(2) 2.1996(17), Ni(1)–P(1) 2.0759(13), Ni(2)–P(2) 2.0739(14), Ni(1)–N(3) 1.939(4), Ni(2)–N(4) 1.944(4), Ni(1)–P(3) 2.1551(16), Ni(2)–P(4) 2.1584(18), P(1)–N(3) 1.556(4), P(2)–N(4) 1.551(4); P(3)–Ni(1)–Cl(1) 95.64(7), N(3)–Ni(1)–Cl(1) 105.27(13), P(1)–Ni(1)–N(3) 45.44(12), P(1)–Ni(1)–P(3) 113.76(6), P(4)–Ni(2)–Cl(2) 95.24(7), N(4)–Ni(2)–Cl(2) 105.72(13), P(2)–Ni(2)–N(4) 45.27(12), P(2)–Ni(2)–P(4) 113.91(6).

lacyclic P–N bonds [av. 1.555(5) Å] are substantially shorter than in pristine **C** [1.664(3) Å],[6] and consistent with P=N double bonds. This electron distribution places a formal negative charge on the phosphorus atoms, thereby reversing the polarity in the phosphorus–nitrogen bonds. The very short Ni–P [av. 2.0796(9) Å] and normal Ni–N [av. 1.925(3) Å] bonds reflect this as well, suggesting that canonical form **D** best describes the bonding in these mono- and di-nuclear species. The title compounds are thus planar, 16-electron nickel(II) complexes with anionic four-electron P=N ligands.



D



E

Only two nickellaazaphosphiranes have previously been structurally characterized, but in these nickel(0) species (**E**) the iminophosphine is a neutral π-donor ligand.[7] Diagnostic for this type of coordination is the lengthening of the P=N bond from 1.544(4) Å[8] in the free iminophosphine to 1.646(2) Å in the complexes, as would be expected from the removal of π-bonding electron density. The nickel–phosphorus bonds in such compounds are also substantially longer [2.23(1)–2.409(3) Å] than those in **2** and **3**.

Nickellaazaphosphiranes with anionic P=N moieties have, to our knowledge, not been fully characterized, although their existence has been confirmed by NMR spectroscopy.[9] The closest crystallographically characterized analogue of the title compounds is a zirconium phosphinomethanide complex with a three-membered P–Zr–C ring, the $P{=}CR_2$ unit being iso-electronic with P=NR.[10]

The easy syntheses and remarkable stabilities of these three-membered metallacycles suggest that it may be possible to extend these metallations to related heterocyclic and perhaps even acyclic primary aminophosphines. Despite their unexpected structures, **2** and **3** exhibit the expected reactivity and are readily alkylated. They may thus still serve as the targeted neutral, single-component catalysts. Our investigations into the generality of these metallaazaphosphirane formations and potential uses of the title compounds in olefin catalysis are continuing.

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Notes and references

‡ Anal. Found for **2**: C, 52.46; H, 9.96; N, 6.64. Calc. for $C_{28}H_{63}ClN_3NiOP_3$: C, 52.15; H, 9.85; N, 6.52%. Mp 176–179 °C. δ_H (C_6D_6, 298 K) 1.626 (9 H, s), 1.592 (30 H, s), 1.349 [6 H, q, *J*(HH) 7.0 Hz], 1.200 (9 H, s, NBu^t), 0.918 [9 H, t, *J*(HH) 7.4 Hz]. δ_C (C_6D_6, 298 K) 76.82 [d, *J*(PC) 8.8 Hz], 54.25 [d, *J*(PC) 27.5 Hz], 53.08 [dd, *J*(PC) 7.6, 3.1 Hz], 32.79 [d, *J*(PC) 4.1 Hz], 32.33 [t, *J*(PC) 5.6 Hz], 31.30 [d, *J*(PC) 8.8 Hz], 27.09 (s), 25.94 [dd, *J*(PC) 25.5, 1.7 Hz], 25.01 [d, *J*(PC) 12.9 Hz], 14.25 (s). δ_P (C_6D_6, 298 K) 109.6 [d, *J*(PP) 24.7 Hz, PO], 15.2 [d, *J*(PP) 85.3 Hz, PBu^n_3], −53.6 [dd, *J*(PP) 84.2, 24.7 Hz, P=N].

Anal. Found for **3**: C, 51.29; H, 10.16; N, 5.97. Calc. for $C_{40}H_{90}Cl_2N_4Ni_2P_4$: C, 51.15; H, 9.66; N, 5.96%. Mp 164 °C. δ_H (C_6D_6, 298 K) 1.88 (18 H, s, NBu^t), 1.67 (12 H, m, Bu^n), 1.52 (12 H, m, Bu^n), 1.46 (18 H, s, NBu^t), 1.35 [12 H, q, *J*(HH) 7.2 Hz, Bu^n], 0.89 [18 H, t, *J*(HH) 7.3 Hz, Bu^n]. δ_C (C_6D_6, 298 K) 54.97 (s, NBu^t), 53.84 [t, *J*(PC) 14.1 Hz, NBu^t], 32.95 (s, NBu^t), 32.70 [t, *J*(PC) 4.6 Hz, NBu^t], 27.21 (s, Bu^n), 25.05 [d, *J*(PC) 11.9 Hz, Bu^n], 24.45 [d, *J*(PC) 25.0 Hz, Bu^n], 14.12 (s, Bu^n). δ_P (C_6D_6, 298 K) 12.19 [dm, *J*(PP) 84.5 Hz, PBu^n_3], −82.43 [dt, *J*(PP) 85.4, 21.6 Hz, P=N].

§ *Crystal data*: for **2**: $C_{28}H_{63}ClN_3NiOP_3$, M = 644.88; orthorhombic, space group *Pnma*, a = 20.538(2), b = 13.6862(15), c = 13.1024(14) Å, U = 3682.8(7) Å^3, T = 212 K, Z = 4, μ(Mo-Kα) = 0.753 mm^{-1}. 24068 reflections measured, 4736 unique (R_{int} = 0.0355) which were used in all calculations. The final $wR(F^2)$ was 0.1549 (all data). For **3**: $C_{40}H_{90}Cl_2N_4Ni_2P_4$, M = 939.36; monoclinic, space group $P2_1/c$, a = 13.905(3), b = 18.186(4), c = 21.592(4) Å, β = 98.13(3)°, U = 5405.3(19) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 0.942 mm^{-1}. 8647 reflections measured, 7028 unique (R_{int} = 0.0876) which were used in all calculations. The final $wR(F^2)$ was 0.1486 (all data).

CCDC reference numbers 166955 and 166956. See http://www.rsc.org/suppdata/cc/b1/b105359k/ for crystallographic data in CIF or other electronic format.

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