Three-co-ordinated Complexes of Cobalt(II) and Nickel(I) Containing Bis-trimethylsilylamino- and Triphenylphosphine-ligands

By D. C. Bradley,* M. B. Hursthouse,* R. J. Smallwood, and A. J. Welch
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary The new three-co-ordinated complexes Co-$[N(SiMe_3)_2]_2(PPh_3)$ and $Ni[N(SiMe_3)_2](PPh_3)_2$ have been prepared, characterized, and their structures determined by *X*-ray crystallography.

With the expectation that cobalt and nickel dialkylamides might be stabilized by phosphines[1] we have explored the reactions of $MCl_2(Ph_3)_2$ (M = Co or Ni) with lithium dialkylamides. Although these reactions have not yielded the desired compounds the corresponding reactions involving $LiN(SiMe_3)_2$ gave rise to the novel three-co-ordinated complexes $Co[N(SiMe_3)_2]_2(PPh)_3$ and $Ni[N(SiMe_3)_2](PPh_3)_2$.

The Co^{II} complex was crystallized from pentane as air-sensitive green crystals (dec. > 90 °C) which gave a mass spectrum containing the parent ion (*m/e*, 641) and several metal-containing fragment ions. Magnetic susceptibility measurements showed it to be a high-spin complex (μ_{eff} = 4·84 B.M. at 298 K).

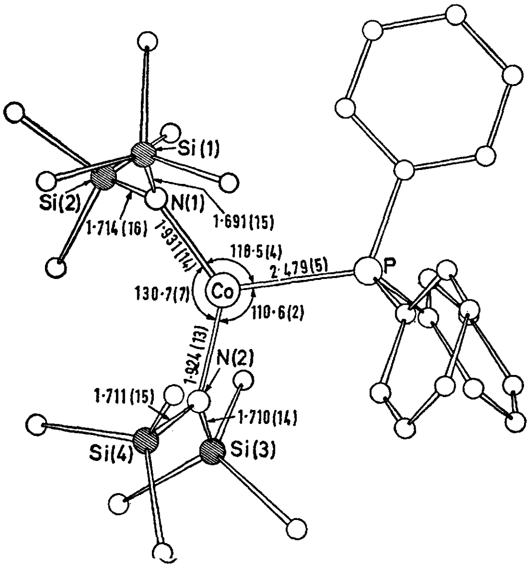

Figure 1. *View of the* $Co[N(SiMe_3)]_2(PPh_3)$ *molecule in a direction perpendicular to the* CoN_2P *mean plane. Angles* (°) *at the nitrogen atoms* (*omitted from the Figure for clarity*) *are:* Co-N(1)-Si(1) 119(1), Co-N(1)-Si(2) 116(1), Si(1)-N(1)-Si(2) 125(1), Co-N(2)-Si(3) 115(1), Co-N(2)-Si(4) 120(1), Si(3)-N(2)-Si(4) 124(1).

The Ni^I complex, obtained as pale-yellow air-sensitive crystals (dec. > 80° C) from benzene, gave μ_{eff} = 1·91 B.M. and in pentane it gave an e.s.r. signal with triplet splitting due to ^{31}P superhyperfine coupling of two equivalent phosphorus atoms ($A^{31}p = 61 \times 10^{-4}\ cm^{-1}$). In view of the rarity of Ni^I compounds[2,3] we have prepared several other bis-phosphinenickel(I) mono-(bis-trimethylsilylamide) complexes (L = PPh_3, $P(Me)_2Ph$, $PMePh_2$, $PEtPh_2$, PEt_2Ph, PEt_3, $L_2 = Ph_2PCH_2CH_2PPh_2$) to demonstrate the generality of this synthesis and to establish the significance of three-co-ordinated Ni^I species.

Since solution molecular weight determinations on air-sensitive compounds containing dissociable ligands are unreliable we have carried out *X*-ray crystal structure analyses.

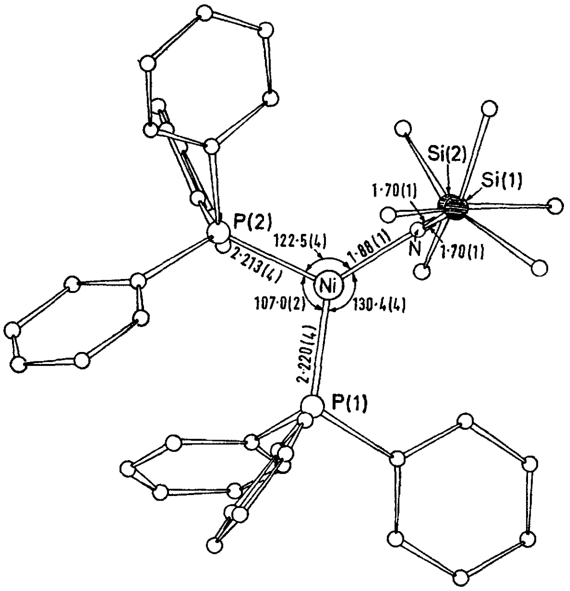

Figure 2. *View of the* $Ni[N(SiMe_3)_2](PPh_3)_2$ *molecule in a direction perpendicular to the* $NiNP_2$ *mean plane. Angles* (°) *at the nitrogen atom are:* Ni-N-Si(1) 117(1), Ni-N-Si(2) 117(1), Si(1)-N-Si(2) 126(1).

$Co[N(SiMe_3)_2]_2PPh_3$, *M* 645·09, triclinic, *a* = 10·17(1), *b* = 13·78(1), *c* = 13·41(1) Å, α = 91·08(10), β = 91·32(10), γ = 94·00(10)°, *U* = 1873 Å^3, D_m *ca.* 1·1, *Z* = 2, D_c = 1·14, $\mu(Cu\text{-}K_\alpha) = 52{\cdot}3\ cm^{-1}$, space group $P\bar{1}$.

$Ni[N(SiMe_3)_2](PPh_3)_2$, *M* 749·73, triclinic, *a* = 9·31(1), *b* = 18·67(1), *c* = 12·27(1) Å, α = 97·87(1·), β = 106·13(10), γ = 91·05(10)°, *U* = 2026 Å^3, D_m *ca.* 1·2 *Z* = 2, D_c = 1·23, $\mu(Cu\text{-}K_\alpha) = 21{\cdot}5\ cm^{-1}$, space group $P\bar{1}$.

Intensity data for both compounds were recorded on a G.E. XRD6 manual diffractometer using the stationary crystal-stationary counter technique and Cu-K_α radiation. For the cobalt compound 2741 reflections out of a total of 3150 measured up to a 2θ value of 90° had significant intensities. For the nickel compound, 3459 out of 4118 reflections measured out to 2θ = 100° were significant.

Both structures were solved by Patterson and Fourier techniques, and refined by full-matrix least-squares. Current *R* values are *ca.* 0·11 for the cobalt compound, and *ca.* 0·09 for the nickel compound. The analyses confirm the three-co-ordinate nature of both compounds, as can be seen from the Figures, which show the metal nitrogen, silicon, phosphorus and carbon atoms. There are no unusually short contacts between the metal atoms and the hydrogen atoms on the α-carbons of the phenyl rings.

In view of the relative novelty of this co-ordination geometry, there are few data against which the metal–nitrogen bond lengths can be compared. On the other hand, the N–Si bond lengths in both compounds are as short as, if not shorter than, those in the free ligand.[4] This implies that the type of interaction postulated to occur in the tris-silylamide of iron(III)[5] does not occur here, but this is only to be expected since the *d* orbitals in both Ni^{I} and Co^{II} are more heavily populated.

Nevertheless, the Ni^{I}–N bond length of 1·88 Å does seem to be shorter than one might expect, and it is possible that some other form of interaction is present in this compound, if not in the cobalt derivative.

We thank the S.R.C. for the award of a studentship (to A.J.W.) and a C.A.P.S. award to (R.J.S.) in conjunction with I.C.I. Ltd. (Petrochemicals Division).

(*Received*, 15*th May* 1972; *Com.* 836.)

[1] V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Comm.*, 1966, 507; L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, 1970, **9**, 2350; P. Heimbach, *Angew. Chem.Internat. Edn.*, 1964, **3**, 648; A. D. Allen and C. D. Cook, *Proc. Chem. Soc.*, 1962, 218.

[2] L. Porri, M. C. Gallazi, and G. Vituli, *Chem. Comm.*, 1967, 228; M. L. H. Green and M. J. Smith, *J. Chem. Soc.* (*A*), 1971, 639; C. S. Cundy, and H. Nöth, *J. Organometallic Chem.*, 1971, **30**, 135; S. Otsuka, M. Naruto, T. Yoshida, and A. Nakamura, *J.C.S. Chem. Comm.*, 1972, 396.

[3] B. Corain, N. Bressan, P. Rigo, and A. Turco, *Chem. Comm.*, 1968, 509.

[4] A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. Beagley, D. W. J. Cruickshank, J. J. Monaghan, B. J. Aylett, and J. A. Ellis, *Chem. Comm.*, 1968, 909.

[5] D. C. Bradley, M. B. Hursthouse, and P. F. Rodesiler, *Chem. Comm.*, 1969, 14.