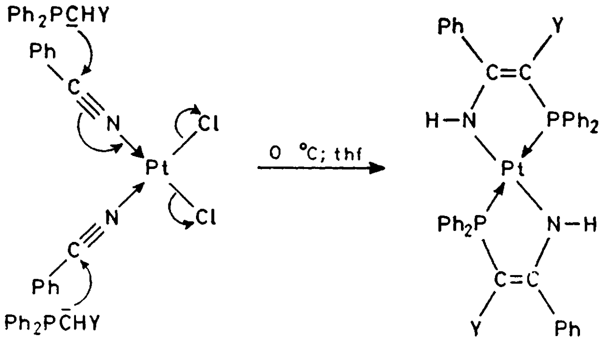
Reaction of α-Phosphino Functional Carbanions with Co-ordinated Nitriles. Synthesis of Bis-chelate (*P*,*N*) Platinum Complexes; *X*-Ray Crystal and Molecular Structure of *trans*-$\overline{\mathrm{Pt[P(Ph)_2C(CO_2Et)C(Ph)N}}\mathrm{H]_2}$

By Pierre Braunstein* and Dominique Matt
(*Laboratoire de Chimie de Coordination, Université Louis Pasteur, 4 rue Blaise Pascal,* F-67070 *Strasbourg Cédex, France*)
and Yves Dusausoy and J. Protas
(*Laboratoire de Minéralogie-Cristallographie, Université de Nancy I, C.O.* 140, F-54037 *Nancy, France*)

Summary The α-phosphino carbanions Ph_2PCHY (Y = CO_2Et or CN) react with the co-ordinated nitrile ligand of *cis*-$Pt(PhCN)_2Cl_2$ to give new bis-chelate (*P*, *N*) platinum complexes $\overline{\mathrm{Pt[P(Ph)_2C(Y)C(Ph)N}}\mathrm{H]_2}$; the structure of one of them (Y = CO_2Et) has been determined by *X*-ray diffraction.

We have reported that functional phosphines of the type Ph_2PCH_2Y (Y = CO_2Et or CN) can form interesting complexes with transition metals.[1] We find that their corresponding carbanions Ph_2PCHY can lead to unexpected structures in reactions with transition metal complexes. It has been shown in the case of Ph_2PCHCO_2Et[2] and Ph_2PCH_2[3] that the phosphino group stabilises the carbanion; the same effect is found here with Ph_2PCHCN.

The carbanions Ph_2PCHY were obtained by a modification of Reetz and Eibach's procedure,[2] using $LiNPr^i(cyclo\text{-}C_6H_{11})$ in tetrahydrofuran (thf) at −5 °C, and their solutions were treated with *cis*-$Pt(PhCN)_2Cl_2$ in thf in a molar ratio of 2:1. Reaction occurs at 0 °C immediately and affords the new yellow-green complexes (**1**) or (**2**) in 55% yield.



(**1**) Y = CO_2Et
(**2**) Y = CN

Although the nitrile ligand is known to be labile, the reaction proceeds by attack of the carbanion on the co-ordinated nitrile ligand with cyclisation through *P* co-ordination. This leads to new (*P*, *N*) three-electron-donor ligands. Microanalytical and spectroscopic data indicate the general formula $\overline{\mathrm{Pt[P(Ph)_2C\ (Y)C(Ph)N}}\mathrm{H]_2}$ for (**1**) and

(**2**) with a bis-chelate structure where the two *P* atoms are *trans* to each other: complex (**1**): ν(C=O) (KBr): 1678w and 1650vs cm^{-1}; ^{31}P n.m.r. δ (CD_2Cl_2; ext. H_3PO_4 ref.) 36 p.p.m., ^{1}J(Pt–P) 2525 Hz; M^+ 943 (^{195}Pt); complex (**2**): ν(C≡N) (KBr): 2170vs cm^{-1}; ^{31}P n.m.r. δ (CD_2Cl_2 ext. H_3PO_4 ref.) 34·5 p.p.m., ^{1}J(Pt–P) 2657 Hz; M^+ 849 (^{195}Pt).

In order to establish conclusively the molecular structure of (**1**), a single-crystal *X*-ray analysis was carried out. Crystals of bis-[β-amino-α-ethoxycarbonylstyryl(diphenyl)-phosphino-*PN*]platinum(II) were obtained from acetone–n-hexane at 0 °C.

Crystal data: $C_{46}H_{42}N_2O_4P_2Pt$; $M = 943{\cdot}9$, monoclinic, $a = 10{\cdot}064(3)$, $b = 23{\cdot}272(3)$, $c = 8{\cdot}964(1)$ Å, $\beta = 77{\cdot}28(1)°$, $U = 2048{\cdot}0(6)$ Å^3, $Z = 2$, $D_c = 1{\cdot}53$ g cm^{-3}, μ(Mo-K_α) = 37 cm^{-1}, space group $P2_1/c$.

The structure was solved by Patterson and Fourier methods[4] using 3163 reflections [$F_0 > \sigma(F_0)$] measured on a Nonius CAD 4 diffractometer [Mo-K_α radiation, $6° < 2\theta < 60°$]. Refinement by full-matrix least-squares (Pt, P, O, N, and C anisotropic, H isotropic) has proceeded to an *R*-factor of 0·047.†

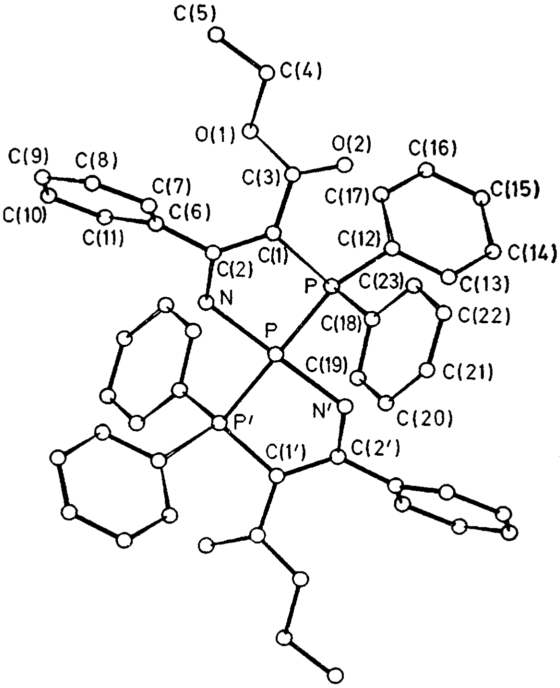
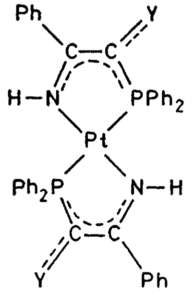


FIGURE. ORTEP drawing of the molecular structure of $\overline{\text{Pt[P(Ph)}_2\text{C(COOEt)C(Ph)NH}}]_2$ (**1**). Principal dimensions are: Pt–N, 1·992(8); Pt–P, 2·280(3); P–C(1), 1·773(9); C(1)–C(2), 1·39(1); N–C(2), 1·32(1); C(1)–C(3), 1·46(1); C(3)–O(1), 1·34(1); C(3)–O(2), 1·21(1) Å; ∠P–Pt–N, 81·0(2); Pt–N–C(2), 124·4(6); Pt–P–C(1), 101·4(3); P–C(1)–C(3), 118·3(7); P–C(1)–C(2), 113·2(7); C(1)–C(2)–N, 119·1(8)°.

The molecular geometry is shown in the Figure, which includes some important bond parameters. The Pt atom lies at the centre of symmetry of the molecule and has a square-planar co-ordination.

The H-shift from C(1) and C(1′) in the carbanion to N and N′ in the complex is shown by i.r. and n.m.r. spectroscopy: ν(N–H) (KBr): 3388mw [complex (**1**)], and 3310mw cm^{-1} [complex (**2**)]; ^{1}H n.m.r. (CD_2Cl_2; Me_4Si): δ(N*H*) 1·74 [complex (**1**)] and 1·57 [complex (**2**)].

Within the metallocycle, the planes Pt,N,C(2),C(1) (maximum deviation 0·005 Å) and Pt,P,C(1) form an angle of 9°. Although there is an angle of 25·3° between the planes Pt,N,C(2),C(1) and C(1),C(3),O(1),O(2), the shortness of the C(2)–N bond [1·32(1) Å], and the relatively low i.r. frequency for the C=O and C≡N groups (*vide supra*) suggest an extensive electron delocalisation within the chelate ligand of the type shown in (A).



(A)

This situation resembles that found recently for a nickel complex containing an isoelectronic (*P,O*) chelating ligand: $(Ph)(Ph_3P)\overline{Ni[P(Ph)_2C(H)C(Ph)O}]$.[5] In our case, the presence of the Y substituent of C(1) (instead of H in the Ni complex) enhances the electron delocalisation.

This appears to be the first reaction of a carbanion with a co-ordinated nitrile.[6] It emphasizes the potential use of α-phosphino carbanions in synthetic co-ordination chemistry.

We thank Dr. F. Mathey for his interest in this work and the Centre National de la Recherche Scientifique for financial support under Greco P.

(*Received*, 9*th May* 1979; *Com.* 486.)

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] P. Braunstein, D. Matt, F. Mathey, and D. Thavard, *J. Chem. Research*, 1978, (*S*) 232; (*M*) 3041.
[2] M. T. Reetz and F. Eibach, *Annalen*, 1977, 242.
[3] D. J. Peterson, *J. Organometallic Chem.*, 1967, **8**, 199; L. Horner, W. D. Balzer, and D. J. Peterson, *Tetrahedron Letters*, 1966, 3315.
[4] W. R. Busing, K. O. Martin, M. A. Levy, R. D. Ellison, W. C. Hamilton, J. A. Ibers, C. K. Johnson, and W. E. Thiessen, 1971, ORX FLS 3, Oak Ridge National Laboratory.
[5] W. Keim, F. H. Kowaldt, R. Goddard, and C. Krüger, *Angew. Chem. Internat. Edn.*, 1978, **17**, 466.
[6] B. N. Storhoff and H. C. Lewis, Jr., *Co-ordination Chem. Rev.*, 1977, **23**, 1.