

methacrylate in 2 and 0.3 h, respectively; 33 and 29 h were required with u.v. irradiation at ca. 27 °C (100 W, quartz); controls of monomer seemed unchanged in all instances.

Reactions presumed to be heterolytic also took place readily. Thus NaBH₄ reduces (3) readily in EtOH to (5) (56%, 10 min). Thionitrites (RSNO) typically thioalkylate thiols (R'SH) to give disulphides (RSSR').^{1,3} In contrast, with (3) and a thiol, equilibration of NO between the two seems to predominate. Thus n.m.r. experiments in CD₃OD suggested that in 24 h a 1:1 molar mixture of (3) and PhCH₂SH gave an equilibrium mixture containing mostly (1). With PhCH₂SH in DMF, PhCH₂SNO was isolated after 24 h in 64% yield as red oil, which then gave (PhCH₂S)₂ in 100% yield; with Ph₃CSH, Ph₃CSNO was isolated in 73% yield. Amines were nitrosated (cf. ref. 1). With *N*-

methylaniline and (3), *N*-methyl-*N*-nitroso-aniline was isolated in 40% yield; with aniline hydrochloride (1.0 equiv.) and HCl (2.5 equiv.), the production of benzenediazonium chloride was shown by isolation of the β-naphthol coupling product [overall from (3), 25%].

We confirm that penicillamine (2) with HNO₂ for 5 h gives 2,2-dimethylthiirancarboxylic acid.⁴ Our finding that a strong green colour develops immediately and persists for ca. 25 min suggests that the thionitrite is a precursor to the diazonium intermediate invoked [cf. (9) of ref. 4].

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A Novel Type of Pt–C Interaction and a Model for the Final Stage in Reductive Elimination Processes Involving C–C Coupling at Pt; Synthesis and Molecular Geometry of [1,*N,N'*-η-2,6-Bis{(dimethylamino)methyl}-toluene]iodoplatinum(II) Tetrafluoroborate

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Summary Square-planar complexes of the type R₂MX (M = Pt or Pd), containing the terdentate ligand 2,6-(Me₂NCH₂)₂C₆H₃, undergo with MeI (M = Pt, X = BF₄) oxidative addition and consecutive reductive elimination resulting in the formation of the complex BF₄⁻ [IPt₂R-Me]⁺ in which the C-aryl centre, at which C–C coupling has occurred, is bonded to the cationic Pt-centre by a novel Pt-to-C-interaction.

THE C-1 and N atoms of the terdentate monoanionic ligand 2,6-(Me₂NCH₂)₂C₆H₃ (I) show a distinct site-preference when bonded to XR₂Sn species. Thus, in trigonal bipyra-

midal 2,6-(Me₂NCH₂)₂C₆H₃SnR₂⁺X⁻, (I) occupies *ax*_N-*eq*_C-

*ax*_N positions, an arrangement imposed by the small angles at Sn in the five-membered chelate rings.^{1,2} As shown by dynamic n.m.r. spectroscopy, pseudorotation processes in

the pentaco-ordinate triorganotin cations are blocked. This is reasonable because then high energy conformers with (I) in *eq*_N-*eq*_C-*ax*_N positions have to be traversed.

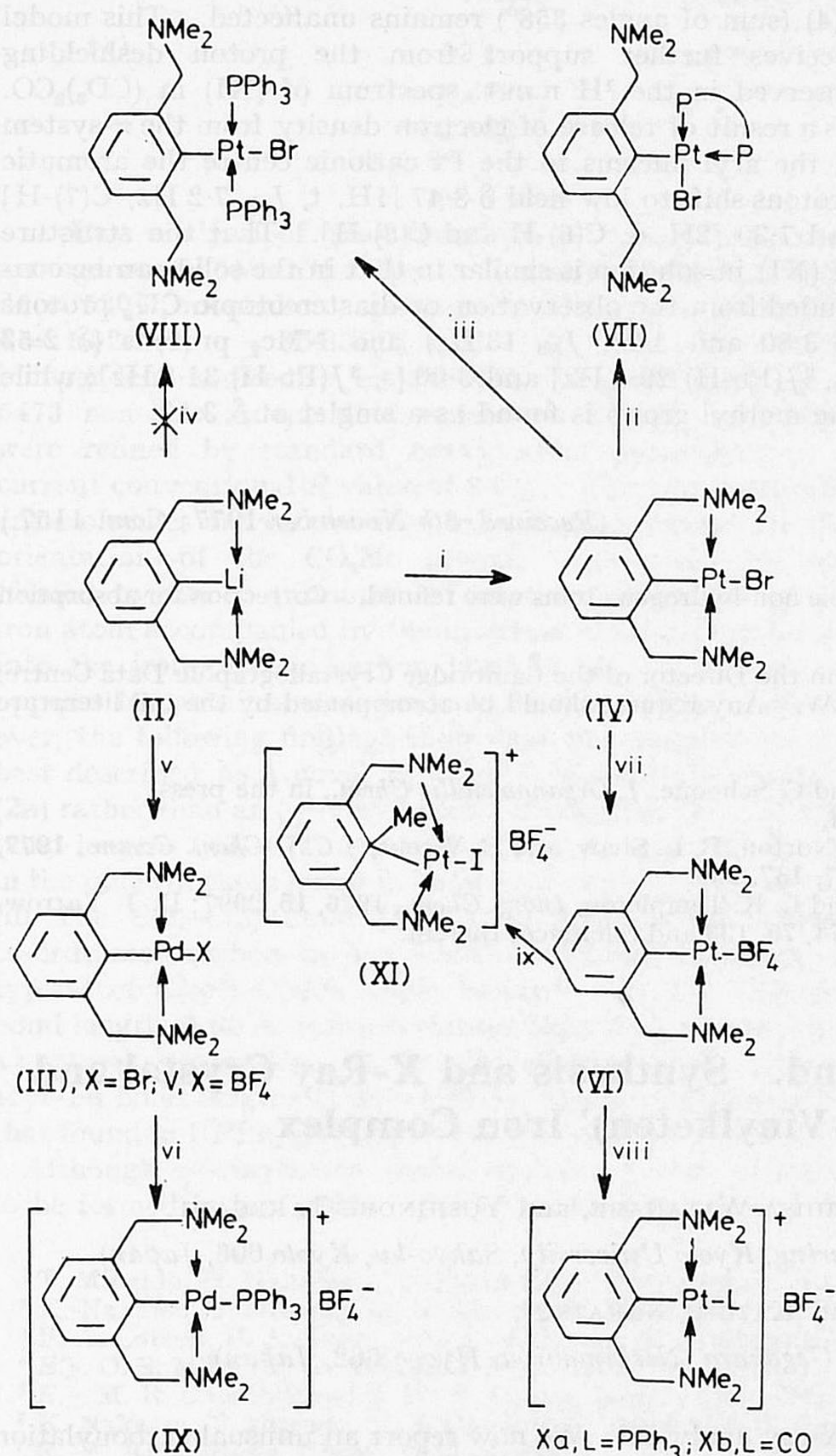
We now report results of a study concerning the influence of the geometric constraint of the terdentate ligand (I) on processes which involve a change of the geometry around a transition metal centre from square-planar to trigonal bipyramidal. These results and those recently reported by Shaw *et al.*³ show that the use of polydentate ligands which, as a result of their specific attachment to the metal, force specific carbon sites into the co-ordination sphere of the metal, gives rise to intriguing transition metal chemistry.

Two different types of Pd and Pt compounds containing (I) have been prepared (cf. Scheme); the halogen complexes (III) and (IV) for which oxidative addition should lead to hexaco-ordinate Pt^{IV} complexes and the BF₄ complexes (V) and (VI) which might yield pentaco-ordinate oxidative addition products. The square-planar structures, in which the N-ligands occupy *trans* positions,† are confirmed by

† Pt–N interaction was confirmed by the observation of ³J(Pt–NMe) and ³J(Pt–NCH₂–) in (IV) (39 and 46 Hz), (VI) (43 and 54 Hz), (Xa) (43 and 54 Hz), and (Xb) (45 and 51 Hz). These couplings are absent in the phosphine complexes (VII) [*cis*-diphosphine, ³¹P n.m.r. δ –3.469 {J(P-1–P-2) 17.2, J(P-1–Pt) 4277 Hz} and –0.045 {J(P-2–Pt) 1638 Hz} p.p.m.] and (VIII) [*trans*-diphosphine, 18.95 {J(Pt–P) 3088 and ⁴J(Pt–CCCH₂N) 11 Hz} p.p.m.].

their n.m.r. resonance pattern and multiplicity as well as by molecular weight data.

Reactions of these compounds with phosphines indicate that the intramolecular N-ligands in (III) cannot be substituted by phosphines whereas similar reactions with (IV) afford the novel phosphine complexes (VII) and (VIII).



SCHEME. i, in the presence of LiBr, (Pr₂S)₂PtCl₂, Et₂O, room temp.; ii, L(-)-diop [2,2-dimethyl-1,3-dioxolan-4,5-bis(methylene)bis(diphenylphosphine)], Et₂O, room temp.; iii, 2 equiv. of PPh₃; iv, (PPh₃)₂PtCl₂, no reaction; v, for X=Br, Br₂Pd(cod), Et₂O room temp. and for X=BF₄, Br₂Pd(cod), Et₂O, room temp., followed by AgBF₄ in acetone; vi, PPh₃, acetone; vii, AgBF₄, acetone, room temp.; viii, PPh₃ or CO; ix, MeI, acetone, room temp. Correct elemental data were obtained for all complexes.

The BF₄ complexes (V) and (VI), however, react with PPh₃ to give the tetraco-ordinate Pd and Pt cationic complexes (IX) and (Xa) in which strong interaction of the metal with the intramolecular N-ligands still exists.

Whereas the compounds (III), (IV), and (V) fail to react, complex (VI) undergoes oxidative addition with MeI under mild conditions (in acetone at room temperature) to give a

ruby-red product (XI) which analyses for 2,6-(Me₂NCH₂)₂-C₆H₃PtMeIBF₄ and decomposes slowly at 175 °C while fast decomposition occurs at 233–235 °C [*M* (cryometry in H₂O) found 312, calc. 615].

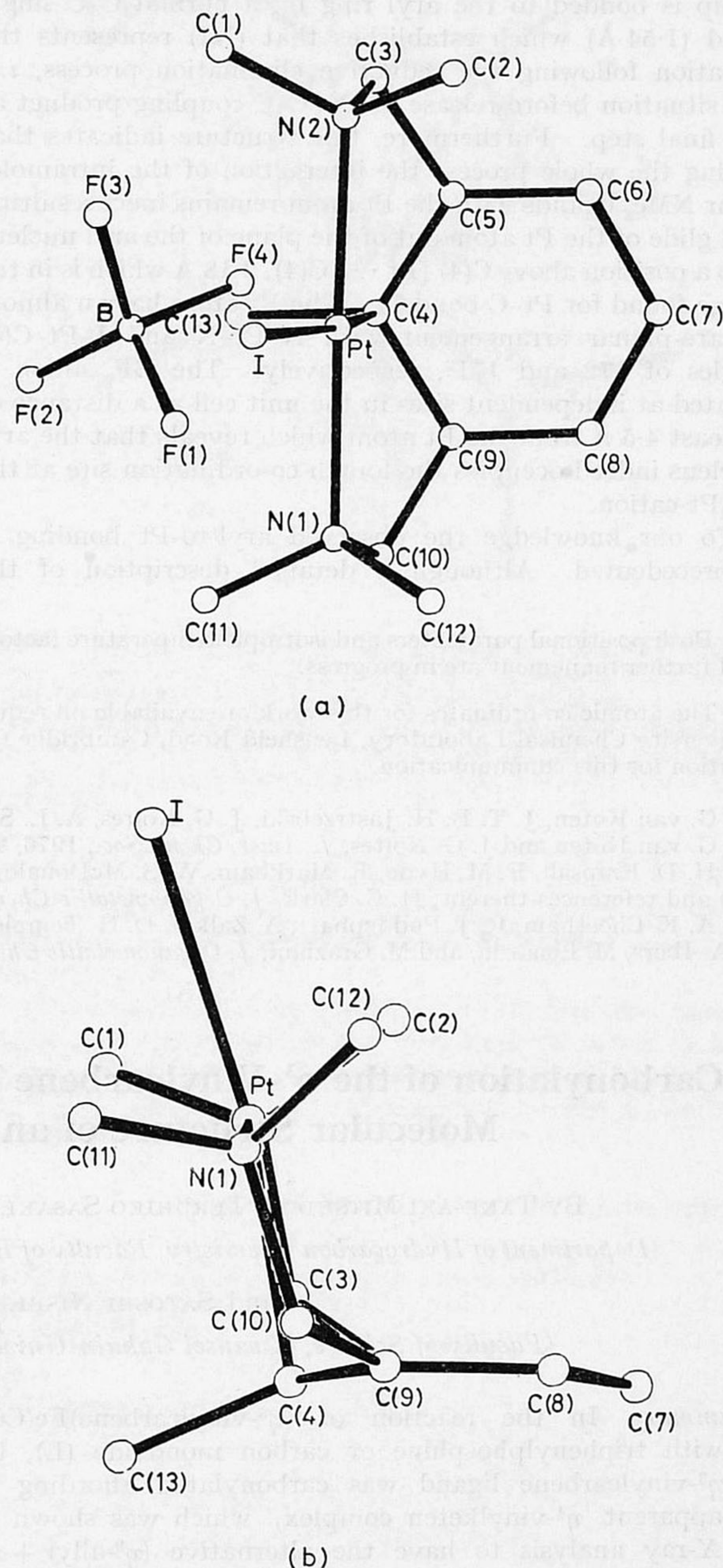


FIGURE. ORTEP drawing of the molecular structure of (XI). Important bond angles and distances are: Pt-N(1), 2.13; Pt-N(2), 2.15; Pt-I 2.58; Pt-C(4), 2.18; C(13)-C(4), 1.54; C(5)-C(4), 1.44; C(4)-C(9), 1.48; C(5)-C(6), 1.39; C(6)-C(7), 1.42; C(7)-C(8), 1.40; and C(8)-C(9), 1.41 Å; ∠Pt-C(4)-C(5), 93; ∠Pt-C(4)-C(9), 87; ∠Pt-C(4)-C(13), 104; ∠C(5)-C(4)-C(9), 114; ∠C(13)-C(4)-C(5) 124; and ∠C(13)-C(4)-C(9), 120°.

Crystal data: (XI), monoclinic, space group P2₁/c; Z = 4; a = 11.033(2), b = 11.553(1); c = 13.915(3) Å; β = 98.34(1)°, U = 1755 Å³. The structure analysis was carried out using 4021 independent reflections of which 523 were < 2.5 σ(I). Intensities were collected on an ENRAF

NONIUS CAD 4 diffractometer using Zr-filtered Mo- K_{α} radiation. The structure was solved by direct methods and refined to a current R -factor of 0.11. ‡§

The structure (see Figure, a) shows that the methyl group is bonded to the aryl ring by a normal C-C single bond (1.54 Å) which establishes that (XI) represents the situation following the reductive elimination process, *i.e.* the situation before release of the C-C coupling product as the final step. Furthermore, this structure indicates that during the whole process the interaction of the intramolecular NMe₂ ligands with the Pt atom remains inert resulting in a glide of the Pt atom out of the plane of the aryl nucleus into a position above C(4) [Pt...C(4), 2.18 Å which is in the range found for Pt-C bonds⁴]. The Pt atom has an almost square-planar arrangement with N-Pt-N and I-Pt-C(4) angles of 172 and 171°, respectively. The BF₄ anion is located at independent sites in the unit cell at a distance of at least 4.5 Å from the Pt atom which reveals that the aryl nucleus indeed occupies the fourth co-ordination site at the IN₂Pt-cation.

To our knowledge the observed aryl-to-Pt bonding is unprecedented. Although a detailed description of the

bonding scheme is not timely, it can be interpreted in terms of an overlap of a component of the e_{1g}, π_3 orbital of the aryl nucleus (at C-1, C-2, and C-6) with an orbital of correct symmetry on Pt. This model explains the considerable bending of the aryl skeleton (see Figure, b) and the lengthening of the neighbouring C(4)-C(5) (1.44 Å) and C(4)-C(9) (1.48 Å) distances. The planar arrangement at C(4) (sum of angles 358°) remains unaffected. This model receives further support from the proton deshielding observed in the ¹H n.m.r. spectrum of (XI) in (CD₃)₂CO. As a result of release of electron density from the π -system of the aryl nucleus to the Pt cationic centre the aromatic protons shift to low field δ 8.47 [1H, t, J_{AB} 7.2 Hz, C(7)-H] and 7.30 [2H, d, C(6)-H and C(8)-H]. That the structure of (XI) in solution is similar to that in the solid can be concluded from the observation of diastereotopic CH₂ protons (δ 3.80 and 4.90, J_{AB} 13 Hz) and NMe₂ protons { δ 2.53 [s, $^3J(\text{Pt-H})$ 29.5 Hz] and 3.00 [s, $^3J(\text{Pt-H})$ 31.5 Hz]} while the methyl group is found as a singlet at δ 3.10.

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‡ Both positional parameters and isotropic temperature factors for the non-hydrogen atoms were refined. Correction for absorption and further refinement are in progress.

§ 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.

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Carbonylation of the η^3 -Vinylcarbene Ligand. Synthesis and X-Ray Crystal and Molecular Structure of an ' η^4 -Vinylketen' Iron Complex

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Summary In the reaction of (η^3 -vinylcarbene)Fe(CO)₃ with triphenylphosphine or carbon monoxide (L), the η^3 -vinylcarbene ligand was carbonylated affording an apparent ' η^4 -vinylketen complex,' which was shown by X-ray analysis to have the alternative (η^3 -allyl + η^1 -acyl)Fe^{II}(CO)₂L structure.

X-ray analysis.² We now report an unusual carbonylation of the η^3 -vinylcarbene ligand of (1) affording an ' η^4 -vinylketen' iron complex and the molecular structure of this complex.

Treatment of (1) with 1 mol. equiv. of triphenylphosphine or carbon monoxide (1 atm) in methylene dichloride at room temperature for several hours gave yellow crystals of (2a) and (2b), respectively,† after evaporation of the solvent, in 78 and 38% yield.

RECENTLY the first example (1) of an (η^3 -vinylcarbene)iron complex was prepared¹ and its structure was established by

† Satisfactory analytical data for the complexes have been obtained. (2a): m.p. 113 °C, M 484; i.r. (CHCl₃) 2020vs and 1968vs; (KBr) 1713 s,br and 1705 m cm⁻¹; ¹H n.m.r. [(CD₃)₂CO, τ , J/Hz] 9.77 [H¹, t, $J(\text{H}^1-\text{H}^2)$ 2.2, $J(\text{H}^1-\text{P})$ 2.2], 7.57 [H², dd, $J(\text{H}^1-\text{H}^2)$ 2.2, $J(\text{H}^2-\text{P})$ 1.0], 6.93 (OMe, s), 6.23 (CO₂Me, s), 2.2—2.8 (Ph, m); ¹³C n.m.r. (δ , Me₄Si, CDCl₃, J/Hz) 24.4 (C⁵, t, $J_{\text{C-H}}$ 163.6), 85.5 (C⁴, s), 103.5 (C³, s), 167.4 (ester C=O, s), 210.0 (Fe-C-O, d, $J_{\text{C-P}}$ 17.1), 214.0 (Fe-C-O, d, $J_{\text{C-P}}$ 12.2), and 241.7 [Fe-C(:O)-, d, $J_{\text{C-P}}$ 7.3] p.p.m. Further detailed spectroscopic data for (2a) and (2b), which are fully in consistent with the X-ray molecular structure, will be reported in a full paper. Expected products such as (*P*-ylide)M(CO)_{*n*} and (vinylcarbene)M(CO)_{*n*}L (H. Fischer and E. O. Fischer, *Chem. Ber.*, 1974, **107**, 673) could not be detected. 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.