Synthesis of O-Co-ordinated Platinum(II) Complexes of Carbonyl-stabilized Arsonium Ylides and the Mechanism of Conversion to their C-Co-ordinated Isomers

Giacomo Facchin,[a] Livio Zanotto,[a] Roberta Bertani,[a] Luciano Canovese[b] and Paolo Uguagliati[b]

[a] *Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., c/o Istituto di Chimica Industriale, Facoltà di Ingegneria, Università di Padova, 35100 Padua, Italy*

[b] *Dipartimento di Chimica, Facoltà di Scienze, Università di Venezia, 30100 Venice, Italy*

The reaction of $[\{PtCl(dppe)\}_2][BF_4]_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] with ylides $Ph_3AsCHCOR$ (R = Me, Ph or OMe) led to novel platinum(II) complexes $[PtCl(dppe)\{OC(R)CH(AsPh_3)\}]BF_4$ (R = Me **1**, Ph **2** or OMe **3**) in which the carbonyl stabilized arsonium ylides are co-ordinated to the metal centre *via* the oxygen carbonyl atom. These derivatives are not stable in chlorinated solvents and slowly undergo isomerization to their C-co-ordinated analogues **4–6** following a first-order rate law. The mechanism proposed for this rearrangement implies both intramolecular and free-ylide promoted intermolecular paths with k_{obs} values of the whole process depending on the basicity of the ylide.

Ylides having a carbonyl group directly attached to the methinic carbon are particularly stable compounds as a consequence of delocalization of negative charge between the ylidic carbon and the carbonyl oxygen atom.[1] Two main effects arise from such charge delocalization: (*i*) carbonyl stabilized ylides are less basic than alkyl- or aryl-substituted ylides; (*ii*) the carbonyl oxygen atom can be potentially involved in direct co-ordination to metal ions. In the co-ordination chemistry of ylides both these effects are important, since they determine the stability of the M–C(ylide) σ bond and the possibility of forming different types of co-ordinated systems. While a large number of organometallic derivatives of carbonyl-stabilized ylides showing co-ordination through the methinic carbon are known,[2] only a few examples of complexes with the alternative O-bonded structure have been described.[3] This latter type of compounds was reported to be stable and no rearrangement to the corresponding C-co-ordinated isomers was observed.

In this paper we report the preparation and characterization of novel platinum(II) complexes of O-co-ordinated stabilized arsonium ylides and a kinetic study of their isomerization to the corresponding C-co-ordinated species.

Experimental

General.—All experiments were done under a nitrogen atmosphere using Schlenk techniques and the solvents were freshly distilled over appropriate drying agents before use. IR spectra were recorded with a Perkin Elmer 983 spectrophotometer. The ^1H and $^{13}C-\{^1H\}$ NMR measurements were made on a Bruker AM-200 spectrometer and $^{31}P-\{^1H\}$ NMR (at 32 MHz) on a Varian FT 80-A spectrometer. Elemental analyses were performed at the Department of Inorganic, Organometallic and Analytical Chemistry of the University of Padua. Melting points were obtained on a hot plate apparatus and are uncorrected.

Materials.—Arsonium ylides were prepared according to the published procedures.[4] The dimer $[\{PtCl(dppe)\}_2][BF_4]_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] was obtained in about 95% yield from equivalent amounts of $[PtCl_2(dppe)]$[5] and $AgBF_4$ (1.0 mol dm^{-3} acetone solution) in CH_2Cl_2 at room temperature for 30 min, followed by filtration to remove AgCl and precipitation with diethyl ether. All the other compounds were commercial grade chemicals and were used as received.

Synthesis of the Complexes.—The O-co-ordinated complexes $[PtCl(dppe)\{OC(R)CH(AsPh_3)\text{-}O\}]BF_4$ (R = Me **1**, Ph **2** or OMe **3**) were synthesised by the same procedure which is described in detail below for **1**. To a solution of $[\{PtCl(dppe)\}_2][BF_4]_2$ (0.358 g, 0.50 mmol) in dichloromethane (25 cm^3), solid $Ph_3AsCHCOMe$ was added in one portion (0.181 g, 0.50 mmol) at 0 °C. On immediate addition of diethyl ether (100 cm^3) to the solution a white solid precipitated which was filtered off, washed with diethyl ether (2 × 20 cm^3) and dried under vacuum. Yield 0.569 g (96%), m.p. 192–194 °C (Found: C, 51.75; H, 4.00. $C_{47}H_{43}AsBClF_4OP_2Pt$ requires C, 52.35; H, 4.00%). IR (Nujol): ν(CO) 1510 cm^{-1}. Complex **2**: yield 0.569 (92%), m.p. 182–184 °C (Found: C, 54.40; H, 3.85. $C_{52}H_{45}AsBClF_4OP_2Pt$ requires C, 54.80; H, 4.00%). IR: ν(CO) at 1503 cm^{-1} in Nujol mull. Complex **3**: yield: 0.479 (80%), m.p. 194–197 °C (Found: C, 51.20; H, 4.05. $C_{47}H_{43}AsBClF_4O_2P_2Pt$ requires C, 51.60; H, 3.95%). IR (Nujol): ν(CO) broad band at *ca.* 1600 cm^{-1}.

The C-co-ordinated complexes $[PtCl(dppe)\{CH(AsPh_3)COR\text{-}C\}]BF_4$ (R = Me **4**, Ph **5** or OMe **6**) were prepared by spontaneous isomerization of their O-co-ordinated counterparts **1–3** in dichloromethane, at room temperature (r.t.), followed by precipitation with diethyl ether, filtration and vacuum-drying. Complex **4**: yield 95%, m.p. 196–198 °C (Found: C, 52.10; H, 4.05. $C_{47}H_{43}AsBClF_4OP_2Pt$ requires C, 52.35, H, 4.00%). IR (Nujol): ν(CO) 1661 cm^{-1}. Complex **5**: yield 92%, m.p. 173–175 °C (Found: C, 54.60; H, 3.90. $C_{52}H_{45}AsBClF_4OP_2Pt$ requires C, 54.80; H, 4.00%). IR (Nujol): ν(CO) 1639 cm^{-1}. Complex **6**: yield 93%, m.p. 208–210 °C (Found: C, 51.30; H, 3.95. $C_{47}H_{43}AsBClF_4O_2P_2Pt$ requires C, 51.60; H, 3.95%). IR (Nujol): ν(CO) 1699 cm^{-1}.

Kinetics.—The isomerization of O- to C-bonded ylide complexes was studied kinetically by monitoring IR spectral changes with time of the ν(CO) band of the C-bonded reaction product in 1,2-dichloroethane at 30 °C, either in the absence or in the presence of free ylide. The kinetic runs were started by quickly dissolving the substrates **1–3** in the prethermostatted solvent or the appropriate solutions of the ylides ($[Pt]_0$ =

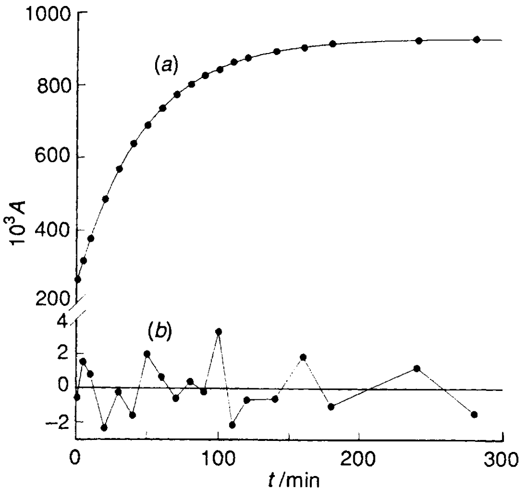


Fig. 1 Non-linear least-squares fit (*a*) and residuals (*b*) of 10^3A *vs.* *t* data to the monoexponential rate law $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$ for the isomerization $\mathbf{1} \longrightarrow \mathbf{4}$ in 1,2-dichloroethane. The increase of the C-bonded ylide ν(CO) band is being monitored

Table 1 Selected NMR data* for [PtCl(dppe){OC(R)CH(AsPh$_3$)}]BF$_4$ **1**–**3** and [PtCl(dppe){CH(AsPh$_3$)COR}]BF$_4$ **4**–**6**

Complex	δ(^{31}P)
1	41.33 [d, ^1J(P^{1}Pt) 3769, ^2J(P^{1}P^2) 7.5, P^1], 32.47 [d, ^1J(P^{2}Pt) 3637, ^2J(P^{1}P^2) 7.5, P^2]
2	40.94 [d, ^1J(P^{1}Pt) 3806, ^2J(P^{1}P^2) 6.0, P^1], 35.19 [d, ^1J(P^{2}Pt) 3660, ^2J(P^{1}P^2) 6.0, P^2]
3	42.16 [d, ^1J(P^{1}Pt) 3700, ^2J(P^{1}P^2) 5.8, P^1], 33.55 [d, ^1J(P^{2}Pt) 3778, ^2J(P^{1}P^2) 5.8, P^2]
4	41.83 [d, ^1J(P^{1}Pt) 3647, ^2J(P^{1}P^2) 3.8, P^1], 41.34 [d, ^1J(P^{2}Pt) 2463, ^2J(P^{1}P^2) 3.8, P^2]
5	40.28 [d, ^1J(P^{1}Pt) 3684, ^2J(P^{1}P^2) 4.6, P^1], 42.01 [d, ^1J(P^{2}Pt) 2508, ^2J(P^{1}P^2) 4.6, P^2]
6	42.96 [d, ^1J(P^{1}Pt) 3677, ^2J(P^{1}P^2) 4.0, P^1] 41.13 [d, ^1J(P^{2}Pt) 2477, ^2J(P^{1}P^2) 4.0, P^2]
	δ(CH)$_{ylide}$
4	4.83 [dd, ^2J(HPt) 85.71, ^3J(HP^1) 5.87, ^3J(HP^2) 9.75]
5	5.73 [dd, ^2J(HPt) 87.30, ^3J(HP^1) 5.09, ^3J(HP^2) 9.90]
6	4.12 [dd, ^2J(HPt) 77.73, ^3J(HP^1) 6.28, ^3J(HP^2) 9.20]
	δ(C)$_{ylide}$
4	54.78 [d, ^1J(CPt) 511.35, ^2J(CP^1) n.o., ^2J(CP^2) 86.20]
5	51.04 [d, ^1J(CPt) 491.16, ^2J(CP^1) n.o., ^2J(CP^2) 85.60]
6	40.80 [dd, ^1J(CPt) 525.10, ^2J(CP^1) 2.68, ^2J(CP^2) 91.55]
	δ(C)$_{carbonyl}$
4	204.60 [s, ^2J(CPt) 26.99, ^3J(CP^2) n.o.]
5	200.34 [d, ^2J(CPt) 28.64, ^3J(CP^2) 3.64]
6	174.82 [d, ^2J(CPt) 36.43, ^3J(CP^2) 4.43]

* Recorded in CDCl$_3$ at room temperature; phosphorus chemical shifts referenced to external H$_3$PO$_4$ (85%); proton and carbon chemical shifts reported from SiMe$_4$ by taking the chemical shift of CDCl$_3$ as δ +7.24 and +77.0, respectively; multiplicity: s = singlet, d = doublet; n.o. = not observed, *J* in Hz; P^1 is the phosphorus *cis* to the co-ordinated ylide; P^2 is the phosphorus *trans* to the co-ordinated ylide.

5×10^{-2} mol dm^{-3}, [ylide]$_0$ = 0–0.2 mol dm^{-3}). The resulting solution was placed in a 0.5 mm thick CaF$_2$ IR cell and IR spectra in the range 1450–1750 cm^{-1} were then recorded at appropriate time intervals, with the cell being placed in a thermostatted environment between each recording and the next. Increasing absorbance values related to the C-bonded ν(CO) band were fitted to the customary monoexponential pseudo-first-order rate law $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, by non-linear regression with A_0, A_∞ and k_{obs} being the parameters to be optimized (Fig. 1) (A_0 = initial absorbance, A_t = absorbance at time *t*, A_∞ = final absorbance). Uncertainties quoted are one standard error of the estimate of the least-squares fit. In the absence of added ylide, the IR spectrum of the reaction mixture at completion was virtually identical with that of the products **4**–**6** prepared independently.

Results and Discussion

Preparation and Spectroscopic Characterization of Complexes.—The dimer [{PtCl(dppe)}$_2$][BF$_4$]$_2$ reacts with the arsonium ylides Ph$_3$AsCHCOR (R = Me, Ph or OMe) in dichloromethane at 0 °C to give the O-co-ordinated complexes **1**–**3** [equation (1)] which are precipitated immediately after mixing of the reactants by addition of a large amount of diethyl ether to the reaction solution (see Experimental section). The three complexes, which are stable in the solid state, where characterized by elemental analysis, IR and ^{31}P-{^{1}H} NMR spectroscopies (see Experimental section and Table 1). Their IR spectra show a carbonyl stretching band at *ca.* 10–15 cm^{-1} lower wavenumber with respect to the free ylides, in accord with co-ordination through the oxygen atom of the carbonyl group. This co-ordination mode is rather rare[3] and up to now unprecedented for platinum systems. The ^{31}P-{^{1}H} NMR spectra support the IR evidence. They display a couple of doublets (with ^{195}Pt satellites) arising from the two magnetically different phosphorus atoms of the diphosphine ligand. The doublet at higher field is attributed to the phosphorus (P^2) *trans* to the O-co-ordinated ylide since it shifts to lower field upon isomerization from O- to C-co-ordination (see below), while the signal of the phosphorus (P^1) *trans* to the chlorine remains virtually unchanged. The values of ^1J(P^{2}Pt) are close to those of ^1J(P^{1}Pt), indicating that the O-co-ordinated ylides and the chlorine atom have similar *trans* influence,[6] while it was shown that a C-co-ordinated carbonyl-stabilized ylide has higher *trans* influence than the chloride ligand.[7,8]

$$\tfrac{1}{2}[\{PtCl(dppe)\}_2][BF_4]_2 + Ph_3AsCHCOR \xrightarrow[0\,°C]{CH_2Cl_2} [PtCl(dppe)\{OC(R)CH(AsPh_3)\}]BF_4 \quad (1)$$

R
1 Me
2 Ph
3 OMe

The O-co-ordinated complexes **1**–**3** are not stable in solution and slowly rearrange to the corresponding C-co-ordinated isomers **4**–**6** [equation (2)]. This transformation can be readily followed by ^{31}P-{^{1}H} NMR spectroscopy. The initial doublets of the O-co-ordinated ylide complexes are replaced by two new doublets in the range δ 40.28–42.96. The ^1J(P^{1}Pt) values for the phosphorus *trans* to the chlorine for complexes **4**–**6** are comparable to those of the corresponding O-co-ordinated isomers, while the ^1J(P^{2}Pt) values are 1200–1300 Hz lower than those of complexes **1**–**3**. This confirms a higher *trans* influence of the C-co-ordinated ylidic ligand. In accord with a C-co-ordination mode to the metal centres,[8,9] the chemical shifts of the ylide protons are found in the range δ 4.12–5.73, *i.e.* at lower field with respect to the free ylides. The ylide methine proton signals in complexes **4**–**6** appear as doublets of doublets due to the coupling with both *cis* [^3J(HP^1) = 5.09–6.28 Hz] and *trans*

$$[PtCl(dppe)\{OC(R)CH(AsPh_3)\}]BF_4 \xrightarrow[r.t.]{CH_2Cl_2} [PtCl(dppe)\{CH(AsPh_3)COR\}]BF_4 \quad (2)$$

R
4 Me
5 Ph
6 OMe

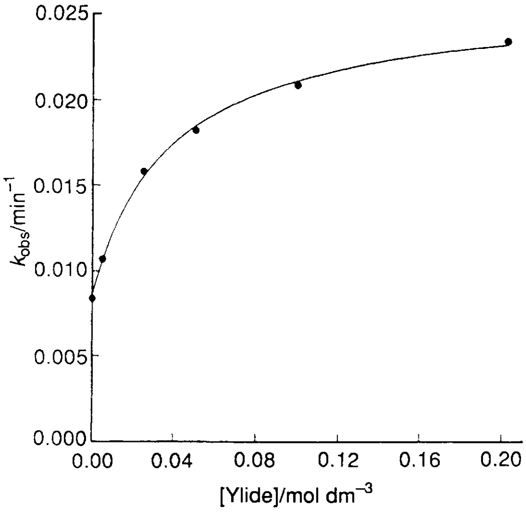


Fig. 2 Non-linear regression of k_{obs} *vs.* [ylide] data [equation (3)] for the isomerization **1** ⟶ **4**

[^3J(HP^2) = 9.20–9.90 Hz] phosphorus atoms of the dppe ligand. The corresponding ^2J(HPt) coupling constants are 85.71, 87.30 and 77.73 Hz, for **4**, **5** and **6** respectively. The ^{13}C-{^{1}H} NMR spectra support C-co-ordination of the ylide in complexes **4**–**6**. The chemical shift of the ylidic carbon lies in the range δ 40.80–54.78, as expected for C-co-ordinated arsonium ylides.[10] The C-co-ordinated ylidic carbon shows coupling with the *trans* P^2 phosphorus [^2J(CP^2) = 85.60–91.55 Hz] and with the ^{195}Pt atom [^1J(CPt) = 491.16–525.10 Hz] but only complex **6** exhibits coupling with the *cis* P^1 phosphorus atom [^2J(CP^1) = 2.68 Hz].

Kinetics and Mechanism of Isomerization.—The kinetics of reaction (2) in 1,2-dichloroethane appears to obey a simple first-order rate law throughout the concentration range of added ylide (0–0.2 mol dm^{-3}), in which pseudo-first-order conditions were assured by the constancy of added ylide concentration, since the reaction under study did not involve consumption of ylide. The k_{obs} values for the isomerisation **1** ⟶ **4** fit the curvilinear rate equation (3) with k_1 = (8.5 ± 0.3) × 10^{-3}

$$k_{obs} = (k_1 + k_2K_e[\text{ylide}])/(1 + K_e[\text{ylide}]) \qquad (3)$$

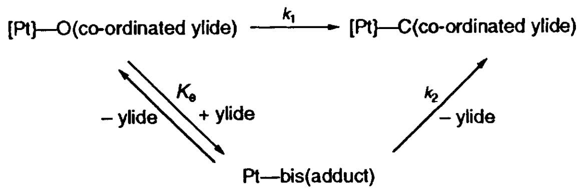
min^{-1}, k_2 = (2.59 ± 0.05) × 10^{-2} min^{-1} and K_e = 26 ± 3 dm^3 mol^{-1} (Fig. 2). In the case of the isomerization **2** ⟶ **5**, a linear rate law was observed [equation (4)] with k_1 = (1.96 ±

$$k_{obs} = k_1 + k_2'[\text{ylide}] \qquad (4)$$

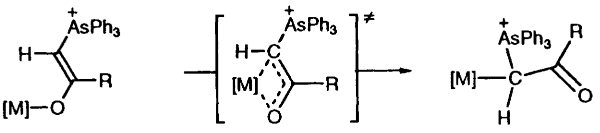
0.01) × 10^{-3} min^{-1} and k_2' = (8.4 ± 0.1) × 10^{-3} dm^3 mol^{-1} min^{-1}. This rate law may be taken as a limiting case of the more general law (3) with K_e[ylide] ≪ 1.

Unfortunately, isomerization **3** ⟶ **6** could not be studied kinetically in the presence of free ylide, since it appeared to be complicated by further, unknown ylide-dependent reactions. Therefore, only the k_1 term could be determined [k_1 = (1.3 ± 0.2) × 10^{-2} min^{-1}].

A simple mechanism that will account for these findings is shown in Scheme 1.



Scheme 1



The k_1 path can be interpreted as a direct intramolecular isomerization of the O-co-ordinated substrate, which is apparently favoured by increasing the basicity of the ylide in accord with the fact that an increased electron density on the methinic carbon of the ylide is expected to lower the activation energy of formation of the metal-ylide carbon bond.

Correlation between basicity (pK_a), structure, and reactivity was already observed for the analogous carbonyl-stabilized phosphonium ylides.[11–13] In this context, it is worth mentioning that in the reactions of phosphonium ylides $Ph_3PCHCOR$ with [{PtCl(dppe)}$_2$][BF$_4$]$_2$, the O-co-ordinated ylide complexes are obtained for R = Me or Ph which are stable towards Pt–O(ylide) to Pt–C(ylide) isomerization, whereas only the Pt–C(ylide) bonded isomer can be isolated with R = OMe.[14] It is apparent that in governing the metal–ylide co-ordination mode, steric effects as well as electronic factors play an important role, as they are related to the bulkiness of the onium group bonded to the ylide methinic carbon. In the mechanism of Scheme 1, the ylide-dependent path can be envisaged as a rapid equilibrium (K_e) process leading to the formation of a labile metal–bis(ylide) adduct. The entering ylide can form a M–O(ylide)[–C(ylide)] or M–O(ylide)[–O(ylide)] adduct depending on its co-ordination mode. The subsequent rate-determining elimination of the O-co-ordinated ylide from M–O(ylide)[–C(ylide)] species produces the final stable C-co-ordinated complex (k_2). In other words, this path might be taken as an isomerization promoted or mediated by the 'free' ylide. Unfortunately, when K_e[ylide] ≪ 1, as in the case of R = Ph, only the combined product $k_2' = k_2K_e$ can be obtained from analysis of rate data, according to equation (4). Apparently, on going from R = Ph to R = Me, the equilibrium constant K_e increases with increasing basicity of the ylide, in agreement with a more extensive formation of a bis(ylide) 'adduct' (in this context, we assume the relative basicities of our arsonium ylides to parallel those of the corresponding phosphonium analogues[11,13,15] since attempts at determining the pK_a values of their conjugate acids by potentiometric titrations were unsuccessful, due to the high basicities involved combined with slow keto–enol equilibria).

References

1 L. Weber in *The Chemistry of the Metal-Carbon Bond*, eds. F. R. Hartley and S. Patai, Wiley, Chichester, 1982, vol. 1, p. 91.
2 H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 907; W. C. Kaska, *Coord. Chem. Rev.*, 1983, **48**, 1.
3 R. Uson, J. Fornies, R. Navarro, P. Espinet and C. Mendivil, *J. Organomet. Chem.*, 1985, **290**, 125; J. A. Albanese, D. L. Staley, A. L. Rheingold and J. L. Burmeister, *Inorg. Chem.*, 1990, **29**, 2209.
4 J. B. Hendrickson, R. E. Spenger and J. J. Sims, *Tetrahedron*, 1963, **19**, 707; N. A. Nesmeyanov, V. V. Pravdina and O. A. Reutov, *Proc. Acad. Sci. USSR*, 1964, **155**, 424; A. W. Johnson and H. Schubert, *J. Org. Chem.*, 1970, **35**, 2678.
5 G. Booth and J. Chatt, *J. Chem. Soc. A*, 1966, 636.
6 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.
7 K. Itoh, M. Fukui and Y. Ishii, *J. Organomet. Chem.*, 1977, **129**, 259.
8 G. Facchin, R. Bertani, M. Calligaris, G. Nardin and M. Mari, *J. Chem. Soc., Dalton Trans.*, 1987, 1381; G. Facchin, R. Bertani, L.

Zanotto, M. Calligaris and G. Nardin, *J. Organomet. Chem.*, 1989, **366**, 409.

9 H. Koezuka, G. Matsubayashi and T. Tanaka, *Inorg. Chem.*, 1976, **15**, 417; E. T. Waleski, jun., J. L. Silver, M. D. Jansson and J. L. Burmeister, *J. Organomet. Chem.*, 1975, **102**, 365.

10 G. Fronza, P. Bravo and C. Ticozzi, *J. Organomet. Chem.*, 1978, **157**, 299.

11 S. Flizar, R. H. Hudson and G. Salvadori, *Helv. Chim. Acta*, 1963, **46**, 1580.

12 M. M. Kayser, K. L. Hatt and D. L. Hooper, *Can. J. Chem.*, 1991, **69**, 1929.

13 P. Uguagliati, L. Canovese, G. Facchin and L. Zanotto, *Inorg. Chim. Acta*, 1992, **192**, 283.

14 G. Facchin, R. Bertani and L. Zanotto, unpublished work.

15 A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, 1963, **85**, 2790; G. Aksnes and J. Songstad, *Acta Chem. Scand.*, 1964, **18**, 655; N. A. Nesmeyanov, V. V. Mikulshina and O. A. Reutov, *J. Organomet. Chem.*, 1968, **13**, 263.

Received 18*th May* 1993; *Paper* 3/02812G