Journal of Organometallic Chemistry, 216 (1981) C25—C28
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CHEMISTRY OF METAL-DIENE COMPLEXES; A DIRECT, NEW PREPARATIVE ROUTE TO HYDRIDO-PLATINUM(II) COMPLEXES

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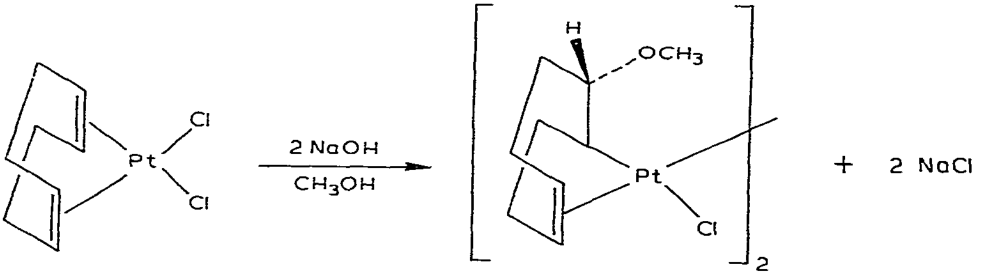
(Received November 13th, 1980)

Summary

A new preparative route to hydrido-platinum(II) complexes, particularly those containing bulky phosphines which are inaccessible by other methods, involves the convenient reaction of phosphines with bis[(2-methoxy-5-cyclooctenyl)chloroplatinum] in methanol. A β-hydrogen elimination mechanism is described, as well as the preparation and use as hydrogenation catalysts of the complexes *trans*-[(2-CH_3O-5-C_8H_{12})Pt(L)Cl] where L = tertiary phosphine.

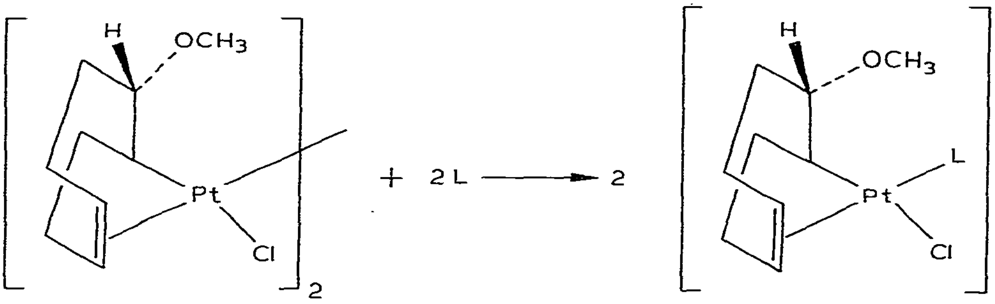
The chemistry of cyclooctadiene complexes of metals, notably of rhodium [1—4], has been extensively studied because of potential applications in catalysis [5]. There have been less detailed studies of analogous platinum complexes, although the complexes (COD)PtX_2 (COD = 1,5-cyclooctadiene) have been widely used in synthesis and their reactions with nucleophiles have been studied [6]. Also, the recent preparation of dicyclooctadieneplatinum(0) by Stone et al. [7] provides an alternative preparative route to low coordinate Pt^0 complexes of the type PtL_2. We now describe a convenient, new preparative route to hydrido-platinum complexes using bis[(2-methoxy-5-cyclooctenyl)chloroplatinum] which is itself the nucleophilic addition product of the methoxy anion with (COD)$PtCl_2$. None of the usual preparative methods [8, 9] for the hydrides $PtHClL_2$ (L = neutral ligand, e.g. tertiary phosphine) are applicable for a wide range of L and most give only poor yields when the ligands are bulky phosphines. For example, the frequently used hydrazine reduction of $PtCl_2L_2$ often leads to extensive decomposition or, at best, poor yields [10—12]. The method described below is particularly suited to the preparation of platinum(II) hydrides containing bulky ligands.

When a suspension of (COD)$PtCl_2$ (I) in methanol is allowed to react with an equimolar amount of sodium hydroxide in aqueous methanol, a clear solution forms within a few minutes, from which bis[(2-methoxy-5-cyclooctenyl)chloroplatinum] [13] can be isolated (eq. 1). This nucleophilic addition of methoxy anion apparently occurs via *trans* addition to the coordinated diene to give an *exo*-configuration of methoxy relative to the metal [14—18].



(1)

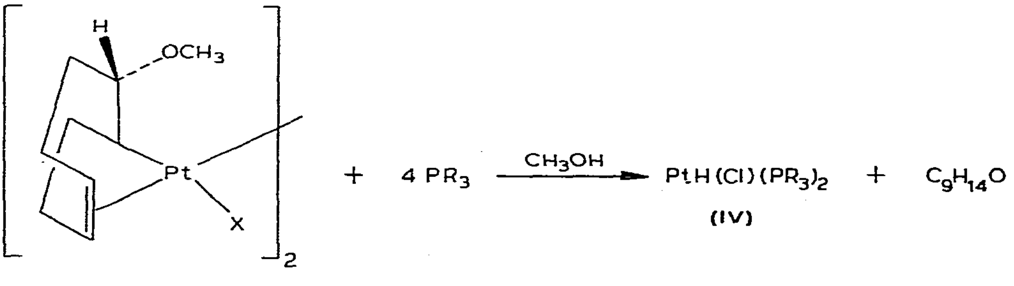
Addition of one equivalent of phosphine per platinum to the solution from reaction 1, or to a benzene solution of II gives the white crystalline complexes *trans*-$PtCl(C_8H_{12}OCH_3)L$ (III). The *trans* geometry, depicted in eq. 2, is based on the large $^{195}Pt—^{31}P$ coupling constants (δ(P) = 23.4—39.4 ppm, *J*(PtP) 4000—4310 Hz) observed in the ^{31}P NMR spectra. These are consistent with a structure containing phosphine *trans* to olefin [19].



(2)

(L = t-$BuPh_2P$; i-Pr_3P, Cy_3P, t-BuMeP, t-Bu_2-n-BuP)

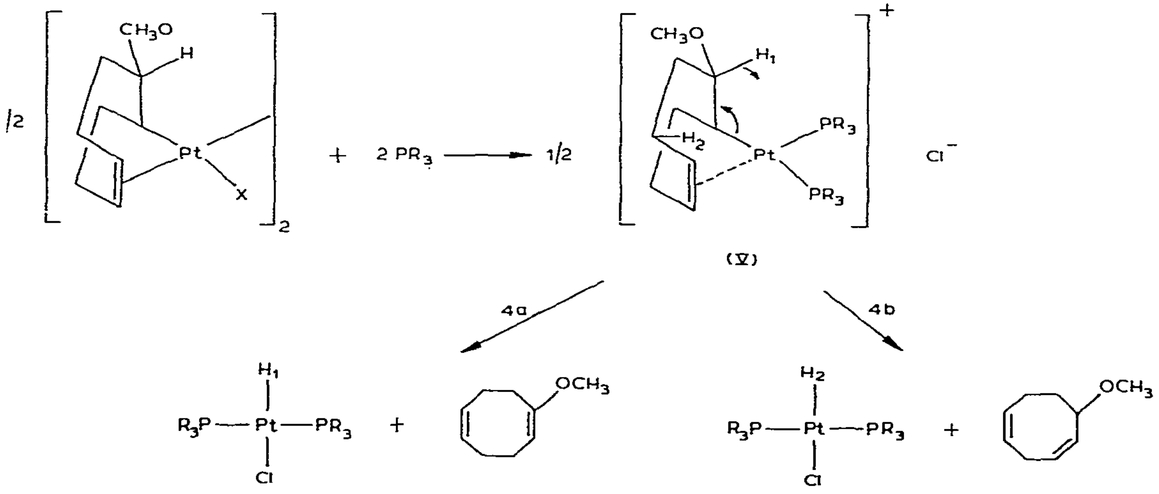
Surprisingly, for L = t-Bu_3P, reaction with II in methanol, instead of giving III, gave *trans*-$PtH(Cl)(PBu\text{-}t_3)_2$ together with 50% recovery of unreacted II. Since this suggested that a further reaction of III with phosphine might be occurring, further reactions in methanol were carried out of II with phosphines (L = t-$BuPh_2P$, i-Pr_3P, Cy_3P, t-Bu_2MeP, t-Bu_2-n-BuP or t-Bu_3P) in 1/4 molar



(3)

ratio, or of III with the corresponding ligand in 1/1 molar ratio. In every case *trans*-$PtH(Cl)L_2$ (IV) was formed quantitatively within a few minutes (eq. 3).

The crystalline products, without recrystallization, are analytically pure, although recrystallization can be carried out from benzene/ethanol/water mixtures. The hydride products have been fully characterized analytically, as well as from infrared (ν(Pt—H) 2175—2370 cm^{-1}), proton NMR spectral data (δ —13.0 to 17.9 ppm; J(P—H) $\approx$12.7 Hz; J(Pt—H) 1000—1250 Hz) and ^{31}P NMR (δ(P) 36.9—75.0 ppm, J(Pt—P) 2950—2800 Hz). It is also noteworthy that while these hydrides are formed by the above reaction in either methanol or ethanol, yields are small or negligible when the reaction is conducted in benzene or hexane. This may indicate the involvement of an ionic intermediate in the reaction. The organic product formed as in eq. 3 was isolated by GLC; its elemental analyses, proton NMR and mass spectral data showed it to be 1,5-methoxycyclooctadiene, $C_9H_{14}O$ (observed m/e = 138.1). A mechanism involving β-hydrogen elimination from the 2-methoxy-5-cyclooctenyl group can then be proposed for platinum hydride formation.



A less likely possibility (eq. 4 b) cannot be ruled out since dienes are known to isomerize [20].

Preliminary observations of similar reactions with $(COD)PdCl_2$ indicate the formation of $PdH(Cl)L_2$ complexes. We also find that the complexes III show considerable activity as catalysts for the hydrogenation of unsaturated hydrocarbons. For example III where L = Cy_3P in the presence of $SnCl_2,2H_2O$ reduces styrene at a hydrogen pressure of 600 psi at 60° C, giving ethylbenzene with approximately 10 000 catalytic turnovers in 2 h.

Acknowledgements. We are grateful for the continued support of this work (to H.C.C.) from the Natural Sciences and Engineering Research Council of Canada.

References

1 R. Spogliarich, G. Zassinovich, G. Mestroni and M. Graziani, J. Organometal. Chem., (1979) 179.
2 G. Zassinovich, G. Mestroni and A. Camus, J. Organometal. Chem., 168 (1979) C37.
3 R.H. Crabtree, A. Gautier, G. Giordano and T. Khan, J. Organometal. Chem., 141 (1977) 113.
4 R. Uson, L.A. Oro, M.A. Garralda, M.C. Claver and P. Lahuerta, Transition Metal Chem., 4 (1979) 55; R. Uson, L.A. Oro, J. Artigas and R. Sariego, J. Organometal. Chem., 179 (1979) 65.
5 B.R. James, Advan. Organometal. Chem., 17 (1979) 319.
6 P.M. Maitlis, The Organic Chemistry of Palladium, Academic Press, New York and London, 1971 and ref. therein.
7 M. Green, D.M. Grove, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1977) 2228 and ref. therein.
8 J. Chatt, L.A. Duncanson, and B.L. Shaw, Proc. Chem. Soc., (1957) 343; J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5075.
9 F.R. Hartley, The Chemistry of Platinum and Palladium, John Wiley and Sons, New York, 1973.
10 P.G. Leviston and M.G.H. Wallbridge, J. Organometal. Chem., 110 (1976) 271.
11 H.C. Clark, A.B. Goel and C.S. Wong, J. Organometal. Chem., 190 (1981) C101.
12 H.C. Clark, A.B. Goel, R.G. Goel and W.O. Ogini, J. Organometal. Chem., 157 (1978) C16.
13 J. Chatt, L.M. Vallarino, and L.M. Venanzi, J. Chem. Soc., (1957) 2496.
14 P.M. Henry, J. Amer. Chem. Soc., 86 (1964) 3246.
15 M. Green and R.I. Hancock, J. Chem. Soc. A, (1967) 2054.
16 R.C. Panattoni, G. Bombieri E. Forsellini, B. Crociano and U. Belluco, J. Chem. Soc. Chem. Commun., (1969) 187.
17 R.N. Haszeldine, R.V. Parish and D.W. Robbins, J. Chem. Soc. Dalton Trans., (1976) 2355 and ref. therein.
18 J. Soulie, J.C. Chottard and D. Mansing, J. Organometal. Chem., 171 (1979) 113.
19 B.F.G. Johnson, T. Keating, J. Lewis, M.S. Subramanian, and D.A. White, J. Chem. Soc. A, (1969) 1793.
20 H. Takahashi and J. Tsuji, J. Amer. Chem. Soc., 90 (1966) 2387.