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Preliminary communication

The preparation of platinum π-olefin complexes from bis(dibenzylideneacetone)platinum(0)

W.J. CHERWINSKI, B.F.G. JOHNSON and J. LEWIS
The Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

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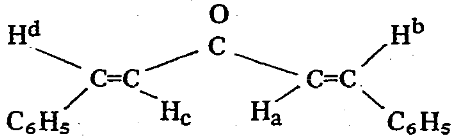
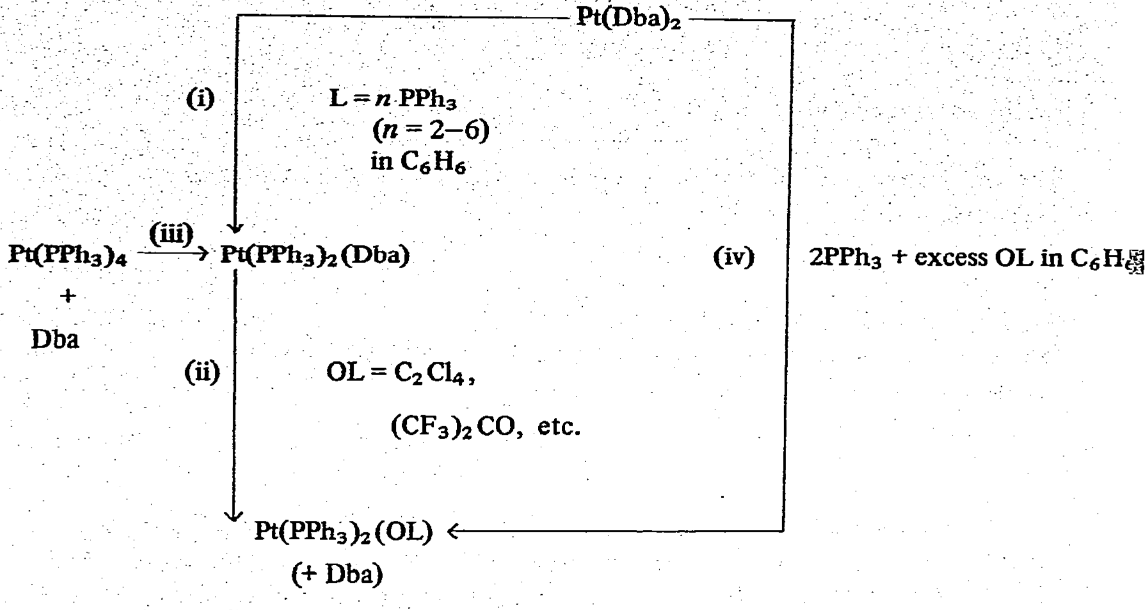
A great many zerovalent metal olefin and acetylene complexes[1] of the type $ML_2(OL)$ have been synthesized and examined where M = Ni, Pd or Pt and L = tertiary phosphine. Typically, for platinum such derivatives have been most common for $L = PPh_3$, owing to the ease of formation and nucleophilic reactivity of the complexes[2] $Pt(PPh_3)_n$ (n = 2, 3 or 4) towards numerous unsaturated substrates. The possible application of ligand displacement as a route to zerovalent platinum derivatives prompted us to investigate reactions of the recently reported air-stable complex[3] bis(dibenzylideneacetone)platinum(0) $Pt(Dba)_2$

Dba =



In the absence of olefins, treatment of a benzene solution of $Pt(Dba)_2$ with an excess of L results in a gradual colour change from purple to orange. From the resulting solutions, air-stable yellow-orange products of stoichiometry $PtL_2(Dba)$, (I) can be isolated for $L = PPh_3$, PPh_2Me and PEt_3. $Pt(PPh_3)_2(Dba)$ could also be formed by reaction of $Pt(PPh_3)_4$ with excess dibenzylideneacetone. Ishii and co-workers[4] have described similar behaviour for $Pd(Dba)_2$ with *N*-donor ligands, although, in a reaction analogous to (i), (Scheme 1), $Pd(PPh_3)_4$ is the major product. For platinum(0), PtL_4 can be isolated from sequence (i) only for the strongly π-acidic ligand $L = AsPh_3$ when $n = 4$, while for $n = 2$, this reaction gives a high yield of (I). The ^1H NMR spectrum of $Pt(PPh_3)_2(Dba)$ in $CDCl_3$: (C_6H_5, H_a), τ2.8 (41H); (H_b), τ4.01 (1H), doublet with $J(H_a{-}H_b)$ 16.5 Hz.; (H_c, H_d), τ5.87 (2H), multiplet with $J(Pt{-}H)$ 55.5 Hz., and its similarity to the spectra of the products of reaction (iii) with benzylideneacetone (Ba) and benzylideneacetophenone (Bap), supports a structure in which the metal is bound by one double bond of dibenzylideneacetone, while the other remains free. For the arsine derivative $J(Pt{-}C_c)$ 275 Hz and



Scheme 1. Preparation of platinum–olefin complexes.

$J(\text{Pt–C}_d)$ 185 Hz. This contrasts to the proposed situation[7] in $Pt(Dba)_2$ where "sideways" coordination is thought to occur through both carbonyl groups. For this latter complex, we have observed no coordinated double bond in the ^{13}C NMR spectrum.

Reactions of the complex $Pt(PPh_3)_2(Dba)$ with activated olefins proceed quantitatively with displacement of Dba affording the known derivatives $Pt(PPh_3)_2(OL)$ where $OL = C_2Cl_4$, CF_3CCCF_3, $(CF_3)_2CO$ or CS_2 (sequence ii). Alternatively, these products may be isolated directly from the reaction of $Pt(Dba)_2$ with excess olefin in the presence of L (sequence iv). Although similar reactions occur for $L = AsPh_3$ and $OL = C_2Cl_4$ and for $L = PPh_2Me$ and $OL = (CF_3)_2CO$ or C_2Cl_4, in no instance does ethylene displace coordinated Dba. When $L = PEt_3$ and $OL = CF_3CCCF_3$, reaction (i) for the yellow-orange oil $Pt(PEt_3)_n(Dba)$ proceeds quantitatively to yield white, crystalline $Pt(PEt_3)_2(CF_3CCCF_3)$ identified by IR, elemental analysis and NMR spectra (^1H and ^{19}F). However, the corresponding complexes $Pt(PEt_3)_2(OL)$ are isolated in low yield where $OL = C_2F_4$ or C_2Cl_4. There is evidence that the white, crystalline compounds which are recovered in quantitative yield for $OL = (CF_3)_2CO$ or $(CF_3)_2CNH$ are products of cyclization of OL with coordinated Dba. The exact nature of these derivatives is currently under investigation.

ACKNOWLEDGEMENTS

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