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π-Cyclopentadienyls of palladium(II) and platinum(II)

R.J. CROSS and R. WARDLE

Chemistry Department, University of Glasgow, Glasgow, W.2 (Great Britain)

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π-Cyclopentadienylnickel compounds of the type $(\pi\text{-}C_5H_5)(R_3P)NiX$ and $(\pi\text{-}C_5H_5)(R_3P)NiR'$ are well known and have been extensively examined[1]. Their preparations have all been based on nickelocene, however, and can not be adapted to form analogous palladium and platinum derivatives. A few π-cyclopentadienyls of divalent palladium and platinum have been reported, but all are either difficult to obtain in good yield or contain organic ligands which limit their versatility in comparison with the nickel compounds[2]. We have prepared $(\pi\text{-}C_5H_5)(Ph_3P)NiCl$ by the action of cyclopentadienylthallium or dicyclopentadienylmercury on phosphinenickel(II) halide complexes and have extended these reactions to palladium and platinum analogues.

Bis(triphenylphosphine)nickel(II) chloride reacts readily with C_5H_5Tl or $(C_5H_5)_2Hg$ at room temperature in various organic solvents to produce the red π-cyclopentadienyltriphenylphosphinenickel(II) chloride in good yield.

$$(Ph_3P)_2NiCl_2 + C_5H_5Tl \rightarrow (\pi\text{-}C_5H_5)(Ph_3P)NiCl + Ph_3P + TlCl$$

$$2(Ph_3P)_2NiCl_2 + (C_5H_5)_2Hg \rightarrow 2(\pi\text{-}C_5H_5)(Ph_3P)NiCl + (Ph_3P)_2HgCl_2$$

Analogous cyclopentadienyls of palladium and platinum were isolated from reactions with binuclear bromo- or iodo-bridged complexes (but not their chlorine analogues) containing only one tertiary phosphine for each metal atom.

$$(Ph_3P)_2Pd_2Br_4 + 2C_5H_5Tl \rightarrow 2(\pi\text{-}C_5H_5)(Ph_3P)PdBr + 2TlBr$$

$$(Et_3P)_2Pt_2I_4 + 2(C_5H_5)_2Hg \rightarrow 2(\pi\text{-}C_5H_5)(Et_3P)PtI + 2C_5H_5HgI$$

Reactions were complete after 30 minutes in tetrahydrofuran at room temperature. These halogen complexes can be converted into σ-bonded organo-derivatives by the action of the appropriate Grignard reagent, but a better method is to start from a substituted compound.

$$(\pi\text{-}C_5H_5)(Et_3P)PdBr + PhMgBr \rightarrow (\pi\text{-}C_5H_5)(Et_3P)PdPh + MgBr_2$$

$$(Et_3P)_2Pt_2Br_2Ph_2 + 2C_5H_5Tl \rightarrow 2(\pi\text{-}C_5H_5)(Et_3P)PtPh + 2TlBr$$

The halogen complexes are green (palladium) or orange (platinum) solids and appear to be indefinitely stable in air at room temperature. The organic derivatives are yellow-orange liquids which partially decompose after long exposure to air. The order of stability of the complexes appears to be Pt > Pd > Ni, resembling that for the series of square-planar complexes $(R_3P)_2MPhCl$. The new compounds are members of new series of palladium and platinum derivatives, which promise to be even more extensive than the analogous nickel series due to the greater stability of the organic complexes. Some physical constants and spectroscopic data are given in Table 1.

TABLE 1

PHYSICAL AND SPECTROSCOPIC DATA

Compound^{a}	Colour	m.p.	$\tau C_5H_5)$	J(P–H) (Hz)	J(Pt–H) (Hz)
$(C_5H_5)(Ph_3P)NiCl$	red	141° (dec.)	5.09^{b}	–	– ref. 1
$(C_5H_5)(Ph_3P)NiPh$	green	134–135° (dec.)	4.97^{b}	–	– ref. 1
$(C_5H_5)(Ph_3P)PdBr$	green	129–130° (dec.)	4.58^{c}	2.5	–^{d}
$(C_5H_5)(Et_3P)PdBr$	green	65–66°	4.47^{c}	2.5	–^{d}
$(C_5H_5)(Et_3P)PdPh$	yellow	–	4.25^{c}	2.0	–^{d}
$(C_5H_5)(Et_3P)PtI$	orange	88–91° (dec.)	4.47^{c}	2.0	19.0^{d}
$(C_5H_5)(Et_3P)PtPh$	yellow	–	4.25^{c}	1.5	12.0^{d}
$(C_5H_5)(n\text{-}Bu_3P)PtCOPh$^{e}	orange	–	4.30^{c}	1.5	13.0^{d}

[a] Satisfactory analyses were obtained for all compounds except $(C_5H_5)(Et_3P)PdPh$, which decomposed during purification. [b] Spectra recorded in CS_2. [c] Spectra in C_6D_6. [d] This work. [e] ν(CO) 1605 cm^{-1}.

Attempts to prepare the cyclopentadienyl complexes of platinum and palladium by the reaction of cyclopentadienylthallium or dicyclopentadienylmercury and $(R_3P)_2MX_2$ [M = Pd, Pt; R = Ph, Et; X = Cl, Br, I] led to decomposition. Decompositions also resulted when phosphine was added to solutions of the π-cyclopentadienyl compounds. We believe that conversion to a σ-bonded cyclopentadienyl is the first step in this breakdown.

$$(\pi\text{-}C_5H_5)(R_3P)PdBr + R_3P \rightleftharpoons [(R_3P)_2Pd(\sigma\text{-}C_5H_5)Br] \rightarrow \text{decomposition}$$

Similar $\pi \rightarrow \sigma$ conversions are thought to operate in the reactions of nickelocene with phosphines[3]. This behaviour contrasts sharply with that of $(\pi\text{-}C_5H_5)(R_3P)NiX$, however, where excess phosphine does not lead to decomposition but may give ionic complexes[4]. σ-Bonded cyclopentadienylplatinum complexes are known to be unstable above 0°[5].

The failure of chloro-bridged binuclear platinum derivatives to give cyclopentadienylplatinum complexes has been reported before[6], and this seems to be a characteristic of these compounds as they also fail to give phenyl derivatives with Grignard reagents[7]. Diphenylmercury and $(Et_3P)_2Pt_2Cl_4$ also lead to decomposition, although Ph_2Hg reacts smoothly with mononuclear complexes[8].

A strong infrared band characteristic of π-bonded cyclopentadienyls[9] is found near 770 cm^{-1} in the palladium complexes and near 798 cm^{-1} in those of platinum.

Nuclear magnetic resonance data are summarised in Table 1. It is interesting to note that the cyclopentadienyl proton resonance is split into a doublet in the Pd and Pt derivatives by coupling to phosphorus. No such coupling is found in the spectra of the nickel analogues[1]. The spectra of the platinum complexes are further complicated by coupling to ^{195}Pt (spin ½, 34%).

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