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Preliminary Communication

Cyclometallated derivatives of palladium(II) and platinum(II) derived from 6-t-butyl-2,2′-bipyridine

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Abstract

The synthesis of the cyclometallated derivatives [PdLCl] and [PtLCl] (HL = 6-t-butyl-2,2′-bipyridine) is reported. The deprotonated bipyridine is terdentate through the two nitrogen atoms and a carbon atom of the t-butyl substituent. The new complexes were characterized by ^{1}H and ^{13}C NMR and FAB-MS spectra.

Many cyclometallated derivatives of palladium(II) and platinum(II) arising from substituted pyridines or bipyridines have been described [1]. Most of them involve activation of aromatic or heteroaromatic C–H bonds [2]. Activation of alkyl groups, although not unprecedented [3], is rarer.

Following our reports [4,5] on the synthesis of [ML′X] (HL′ = 6-(1-methylbenzyl)-2,2′-bipyridine; M = Pd and X = Cl, M = Pt and X = Cl or H) where the deprotonated bipyridine is terdentate through the two nitrogen atoms and the carbon atom of the phenyl substituent giving a [5,6]-fused system, here we describe the synthesis of two cyclometallated species [MLCl] (HL = 6-t-butyl-2,2′-bipyridine, M = Pd, **1**, M = Pt, **2**) which involves activation of a CH_3 group.

The ligand HL was prepared from t-butyl nitrile according to a general procedure previously reported [6].

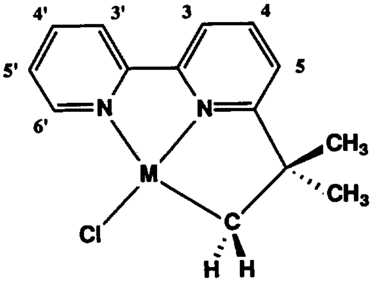
Complexes **1** and **2** were obtained from $Na_2[PdCl_4]$ and $K_2[PtCl_4]$, respectively (reaction (1)).

$$[MCl_4]^{2-} + HL \xrightarrow{H_2O/HCl} [MLCl] \qquad (1)$$

M = Pd, **1**
M = Pt, **2**

The palladium derivate is obtained at room temperature, whereas the synthesis of the platinum analogue requires reflux temperature (**1**, yellow, m.p. 181°C; **2**, orange-yellow, m.p. 210°C). Yields are high (92% and 81% for **1** and **2**, respectively) and no intermediate is trapped under the experimental conditions used.

The microanalysis supports the formulations [MLCl] (**1**: Found: C, 48.08; H, 4.24; N, 7.55; calc.: C, 47.61; H, 4.29; N, 7.93%; **2**: Found: C, 38.52; H, 3.44; N, 6.07; calc.: C, 38.05; H, 3.43; N, 6.34%). The FAB mass spectra (3-nitrobenzyl alcohol as matrix) of each of these complexes exhibit peaks assigned to $[MLCl]^+$ (M = Pd m/z 352, M = Pt m/z 441) and $[ML]^+$ (M = Pd m/z 317, M = Pt m/z 406) with the expected isotopomer distributions. Peaks with very low intensity at m/z 669 (M = Pd) and 847 (M = Pt) can be assigned to dinuclear $[LM(\mu\text{-}Cl)ML]^+$ species, probably arising from interaction of [MLCl] with $[ML]^+$ in the vapour phase.



The formulation of complexes **1** and **2** as monomeric cyclometallated derivatives rests mainly on NMR evidence (room temperature) *. Activation of a CH_3 group is clearly deduced from the ^{1}H and ^{13}C spectra (CD_2Cl_2) (^{1}H: δ, CH_2 2.53 s, **1**, 2.68 s, **2**; ^{13}C: δ, CH_2 34.9, **1**, 19.1 **2**). The assignment of the CH_2 resonances in the ^{13}C spectra has been confirmed by a Heteronuclear (^{13}C–^{1}H) Chemical Shift Correlation Experiment (HETCOR). For complex **2**, as expected, coupling to ^{195}Pt ($I = 1/2$, natural abundance *ca.* 34%) is observed: $^{2}J(Pt\text{–}H) = 84.3$ Hz, $^{1}J(Pt\text{–}C) = 746$ Hz. Coupling of H(6′) to ^{195}Pt ($^{3}J(Pt\text{–}H) = 11$ Hz) gives evi-

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* ^{1}H NMR data (CD_2Cl_2). Compound **1**: δ 1.43 CH_3 (s, 6H); 2.53 CH_2 (s, 2H); 7.28 + 7.86 H(5) + H(3) (dd + dd, 2H); 7.58 H(5′) (m, 1H); 7.95 H(4) (t, 1H); 8.02 H(3′) (dd, 1H); 8.08 H(4′) (m, 1H); 8.75 H(6′) (doublet of multiplets, 1H). Compound **2**: δ 1.42 CH_3 (s, 6H); 2.68 CH_2 (s, 2H); 7.24 + 7.77 H(5) + H(3) (dd + dd, 2H); 7.70 H(5′) (m, 1H); 8.05 H(3′) + H(4) (m, 2H); 8.14 H(4′) (td, 1H); 9.10 H(6′) (doublet of multiplets, 1H).

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dence of the coordination of the terminal pyridine ring, at least for compound **2**. Molecular weight determinations in solution ($CHCl_3$) suggest that both **1** and **2** are monomeric and confirm that the bipyridine is terdentate. This rules out alternative formulations of **1** and **2** as dimers having bridging chlorides and *N–C* ligands.

A full analysis of the ^{13}C NMR spectra will be reported elsewhere: HETCOR experiments indicate that coupling to ^{195}Pt of the hydrogen and carbon atoms of the terminal pyridine ring is less than that of the corresponding atoms of the pyridine involved in the cyclometallated ring, possibly as a consequence of the strong *trans* influence of the alkyl ligand.

Work is in progress on the reactivity and the structures of these complexes.

Acknowledgments

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