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Methylpalladium(II) Complexes of Pyrazole and Thioether Donor Ligands

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Organopalladium(II) species RPd(II), $R_2Pd(II)$, and RR'Pd(II) are believed to occur in a wide range of catalytic systems of importance in synthesis of organic compounds involving coupling to form R–R and R–R' [1, 2]. Although many methylpalladium(II) complexes of phosphorus and arsenic donor ligands have been synthesized [3], reports of complexes containing nitrogen and thioether donor ligands are restricted to the 2,2'-bipyridyl derivatives $Me_2Pd(bpy)$ [4] and Me(X)Pd(bpy) (X = Cl [5], I [6]) and the dithioether derivatives $Me_2Pd(RSCH_2CH_2SR)$ (R = Me, Et) [4]. Simple methyl complexes are of interest as models for intermediates in catalytic systems, and also as models for the synthesis of organic compounds via palladation of organic compounds involving neutral donor ligand directing groups, usually nitrogen donors [1, 3].

We report here initial studies of the synthesis and reactivity of a series of complexes $Me_2Pd(L)$ and Me(I)Pd(L) [L = poly(pyrazol-1-yl)methane ligands pz_2CH_2, $pz_2C(H)Me$, pz_2CMe_2, and pz_3CH], together with the synthesis of $[Me(I)Pd(SMe_2)]_2$.

$$PdCl_2(SMe_2)_2 \xrightarrow[\text{(ii) L}]{\text{(i) 2-3 MeLi(halide free, } -60\ ^\circ\text{C)}} Me_2Pd(L)$$

$$PdCl_2(SMe_2)_2 \xrightarrow[\text{(ii) L}]{\text{(i) 2 MeMgI } (-40\ ^\circ\text{C)}} Me(I)Pd(L)$$

$$PdCl_2(SMe_2)_2 \xrightarrow{\text{2 MeLi/LiI } (-60\ ^\circ\text{C)}} [Me(I)Pd(SMe_2)]_2$$

In a typical synthesis of $Me_2Pd(L)$, 2–3 mol equivalents of halide free methyllithium were reacted with *trans*-$PdCl_2(SMe_2)_2$ at −60 °C in dry diethyl ether under nitrogen until the solution clarified, solid L was added and the solution slowly warmed with stirring to −15 °C, followed by hydrolysis, filtration, separation and drying of the organic layer, filtration, removal of solvent to dryness, and recrystallization of $Me_2Pd(L)$ from dry acetone/hexane at −70 °C. Similar procedures were used for synthesis of Me(I)Pd(L) and $[Me(I)Pd(SMe_2)]_2$, with the latter synthesis employing MeLi containing LiI (prepared from 2Li + MeI in diethyl ether) and isolation of the complex directly from diethyl ether after hydrolysis.

The complexes have satisfactory microanalyses (C, H, N, I, S), infrared, and ^1H NMR spectra. For example, complexes with pz_3CH exhibit variable temperature ^1H NMR spectra, with $Me_2Pd(pz_3CH)$ giving six pyrazole ring resonances at −60 °C in $(CD_3)_2CO$ in the ratio 1:2:2:1:2:1 corresponding to two coordinated rings and one uncoordinated (or weakly coordinated) ring, with coalescence of resonances at higher temperatures consistent with rapid intramolecular exchange of coordinated and uncoordinated rings.

The complex $[Me(I)Pd(SMe_2)]_2$ is assigned a dimeric structure from osmometric molecular weight measurements, giving a value of 679 (Calc. for dimer 621) on initial dissolution in chloroform at 37 °C prior to decomposition. An analogous platinum complex has been detected by ^1H NMR spectroscopy in $CDCl_3$, but could not be isolated [7]. Variable temperature studies and interpretation of ^1H–^{195}Pt coupling allowed assignment of structure as $[Me(\mu\text{-}I)Pt(SMe_2)]_2$, with presence of *cis* and *trans* isomers in rapid equilibrium [7]. The palladium complex, and the analogous chloride, $[Me(Cl)Pd(SMe_2)]_2$, obtained from *trans*-$PdCl_2(SMe_2)_2$ and halide free MeLi, have much simpler spectra, lacking coupling, with MePd(II) singlets [δ 0.76 (Cl), 0.93 (I)] and SMe_2 singlets [2.34 (Cl), 2.37 (I)] in 1:2 ratio, unaltered on cooling to −60 °C in $CDCl_3$. Thus, ^1H NMR spectra do not permit definite assignment of structure.

The complexes Me(I)Pd(L) are quite stable at ambient temperature, $Me_2Pd(L)$ require storage at −20 °C, and the dimethylsulfide complexes slowly decompose over 2–3 months at −20 °C. Preliminary studies of the reactivity of the complexes indicate that $[Me(I)Pd(SMe_2)]_2$, which is readily obtained in 85% yield, may be a suitable reagent for synthesis of methylpalladium(II) complexes, *e.g.* it reacts directly with $pz_2CH(Me)$ and pz_2CMe_2 to form Me(I)Pd(L). The pyrazole complexes may also be suitable for modelling reactions that may be involved in catalytic systems, *e.g.* iodomethane reacts cleanly with $Me_2Pd(pz_2CMe_2)$ to form $Me(I)Pd(pz_2CMe_2)$. Further studies of synthetic applications and reactivity of the complexes are in progress.

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