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Preliminary communication

METALLATION OF TRIS(1-PYRAZOLYL)METHANE BY DIMETHYLPLATINUM(II)

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Summary

Tris(1-pyrazolyl)methane ($HCpz_3$) reacts with $Pt(CH_3)_2(COD)$ to form $Pt(CH_3)_2(HCpz_3)$, and when this complex is heated in pyridine metallation of the pyrazole ring at C(5) occurs to form $Pt(CH_3)(HCpz_2(pzH_{-1}))(py)$. A triphenylphosphine derivative, $Pt(CH_3)(HCpz_2(pzH_{-1}))(PPh_3)_2$, when slowly heated to 185°C forms $Pt(HCpz_2(pzH_{-1}))(C_6H_4PPh_2)$; this complex has both the nitrogen and phosphorus donor ligands metallated to form six and four-membered rings, respectively.

Dimethylplatinum(II) forms square planar complexes with potentially tridentate ligands, e.g. the complex $Pt(CH_3)_2(MeC(CH_2PPh_2)_3)$ has the triphosphine present as a bidentate [1]. Similarly, isoelectronic $Au^{III}(CH_3)_2$ forms square planar complexes, but since the tris(1-pyrazolyl)methane complex $[Au(CH_3)_2(HCpz_3)]NO_3$ has essentially square-planar geometry with an additional weak axial Au···N interaction [2] we have investigated the interaction of this ligand with $Pt(CH_3)_2(COD)$.

Tris(1-pyrazolyl)methane reacts with $Pt(CH_3)_2(COD)$ under reflux in benzene to give $Pt(CH_3)_2(HCpz_3)$ as a white powder. This complex is insufficiently soluble for ^1H NMR spectral studies, and crystals for structural analysis could not be obtained. However, it does dissolve in hot pyridine, and from the cooled solution crystals of the metallated complex $Pt(CH_3)(HCpz_2(pzH_{-1}))(py)$ (B) formed, presumably with loss of methane. Subsequent reactions give the products in Scheme 1, where all reactions in the scheme proceed with high yield and without visible decomposition to metallic platinum. Slow heating of complex C to 185°C in a vacuum gives a sublimate of Ph_3P (infrared identification) and complex D, which can be recrystallized from

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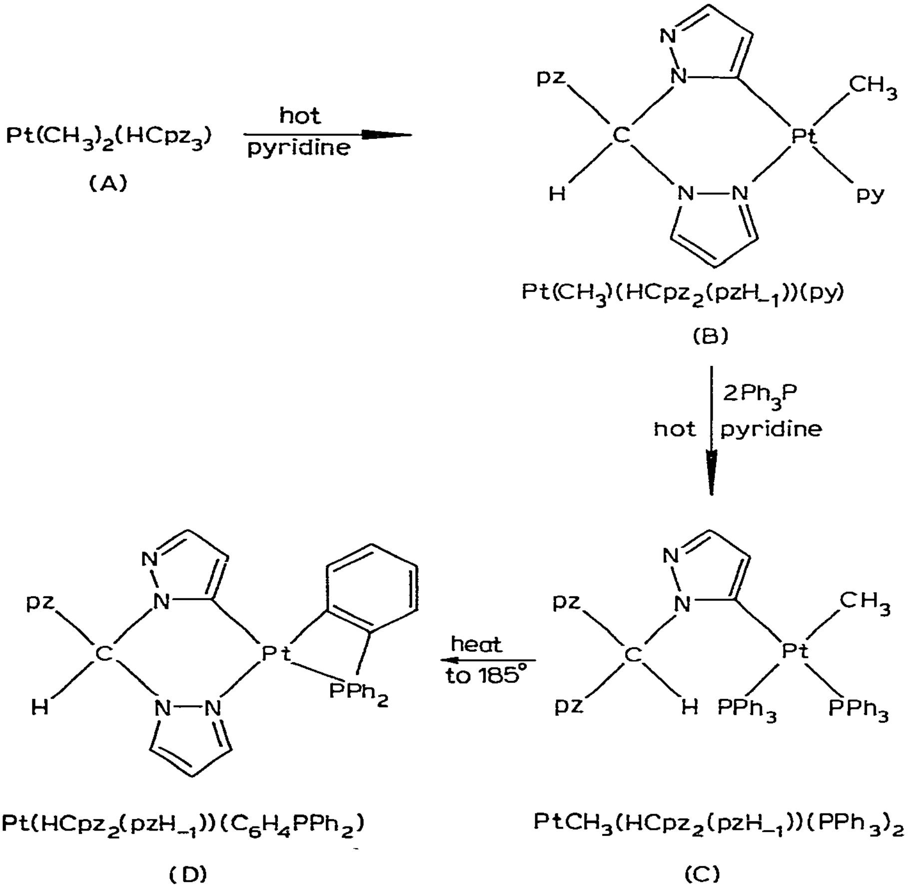
$$\mathrm{Pt(CH_3)_2(COD)} + \mathrm{HCpz_3} \xrightarrow[\text{reflux}]{\text{benzene}} \underset{\text{(A)}}{\mathrm{Pt(CH_3)_2(HCpz_3)}} + \mathrm{COD}$$



$\mathrm{Pt(CH_3)(HCpz_2(pzH_{-1}))(py)}$ (B)

$\mathrm{PtCH_3(HCpz_2(pzH_{-1}))(PPh_3)_2}$ (C)

$\mathrm{Pt(HCpz_2(pzH_{-1}))(C_6H_4PPh_2)}$ (D)

benzene/petroleum ether. Complexes A—D have satisfactory microanalyses (C, H, N), infrared spectra indicate presence of the groups indicated in formulae with absorptions altered from that of the free reagents, and the chloroform soluble complexes C and D are monomeric in this solvent at 37°C (vapour pressure osmometry; C: obs. 905, calcd. mol. wt. 947; D, obs. 689, calcd. mol. wt. 669).

Infrared spectra of complexes A—C, but not D, have bands at 546—584 $\mathrm{cm^{-1}}$ readily assigned as ν(Pt—C) by comparison with previously reported values [3], and complex D has absorptions in the region 700—800 $\mathrm{cm^{-1}}$ and near 1100 $\mathrm{cm^{-1}}$ characteristic of an *ortho*-substituted benzene nucleus as expected [4,5] for metallation of $\mathrm{Ph_3P}$. Raman spectra for the complexes (except C which gives poor spectra due to high fluorescence), together with several pyrazoles, allow assignment of ν(C—H) for the methine group at

2881—2918 cm^{-1}, and thus metallation has not occurred at the methine carbon.

The chloroform soluble complexes C and D have ^1H NMR spectra showing presence of a methyl group in C but not D, and indicate that metallation of $HCpz_3$ occurs at C(5). Thus, C has a complex resonance centred at δ 0.11 ppm, very similar to that shown by $Pt(Me)_2(PPh_3)_2$ [6], and resonances for H(3) and H(4) of the metallated rings occur upfield from H(3) and H(4) resonances of the other pyrazolyl rings. For complex C H(3) and H(4) are clearly resolved as doublets with $J_{3,4} \sim 9$ Hz.

Complexes B—D appear to be the first examples of metallation of tris-(1-pyrazolyl)methane; for B and D cyclometallation involves six-membered rings rather than the usual five-membered rings [4,7], and complex D involves presence of four and six-membered rings in the same complex. As for previous examples of six-membered rings [8] the structure of the ligand precludes five-membered ring formation. An interesting aspect of metallation of $HCpz_3$ is the flexibility of the metallated ligand to act as a simple aryl group ("MC", e.g. complex C), as a bidentate ("MCN", e.g. B and D), or potentially as a tripodal tridentate ("MCN_2") with geometry closely related to that expected in complexes without metallation ("MN_3", e.g. as shown recently for $[Pt(CH_3)(HCpz_3)(CO)]^+PF_6^-$ [9]). For simplicity, the structures of complexes B—D presented in Scheme 1 emphasize the square planar geometry adopted in complexes of $Pt^{II}(Me)_2$ with potentially tripodal phosphine ligands [1].

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