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Preliminary communication

DISPLACEMENT OF NORBORNADIENE (NBD) FROM PtR_2(NBD) (R = Me, CF_3) BY WEAK LIGANDS

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Summary

Norbornadiene (NBD) is more easily displaced from $PtMe_2$(NBD) by other ligands than is cyclooctadiene (COD) from $PtMe_2$(COD). *cis*-$PtMe_2L_2$ (L = py, ½tmen, ½en, NH_3, DMSO) have been prepared in this way. *cis*-$PtMe_2py_2$ is very reactive toward oxidative addition. Pyridine can usually be removed from the platinum(IV) products using acid. NBD is even more readily displaced from $Pt(CF_3)_2$(NBD), giving *cis*-$Pt(CF_3)_2L_2$ (L = py, ½tmen, ½en, NH_3, DMSO, NCR, DMF, CN^-, I^-, $acac^-$). *cis*-$Pt(CF_3)_2py_2$ with CF_3I gives *fac*-$Pt(CF_3)_3py_2I$.

1,5-Cyclooctadiene (COD) is readily displaced from $PtMe_2$(COD) by strongly bonding ligands, L, such as phosphines, arsines, isonitriles, and 2,2′-bipyridyl (bipy), to give *cis*-PtR_2L_2, [1—4], but displacement of COD by other N-donors is difficult, as the heating required to effect the olefin displacement causes decomposition of the product. *cis*-$PtMe_2py_2$ has been reported in 5% yield from the reaction of $PtMe_2$(COD) with pyridine (py) but characterized only by its decomposition point [2]. We have attempted unsuccessfully to reproduce this preparation, although low concentrations of $PtMe_2py_2$ were detected by NMR in the reaction mixture during the reaction.

Because of its smaller 'bite' angle, NBD would be expected to bind less tightly to platinum than COD. This expectation was fulfilled. Pure pyridine instantaneously displaced NBD from $PtMe_2$(NBD) (I) in benzene, to give *cis*-$PtMe_2py_2$ (II), which was isolated as an air-stable, pale yellow solid. Solutions in chloroform are light sensitive, but otherwise stable at 25°C. The ^1H NMR spectrum in $CDCl_3$ showed the expected peaks (δ(Pt—Me) 1.01 ppm, ^2J(Pt—CH_3) 84.2 Hz).

Clark and Manzer [1] reported the preparation of $PtMe_2$(tmen) from $PtMe_2$(COD) and *N,N,N′,N′*-tetramethylethylenediamine (tmen). In our hands,

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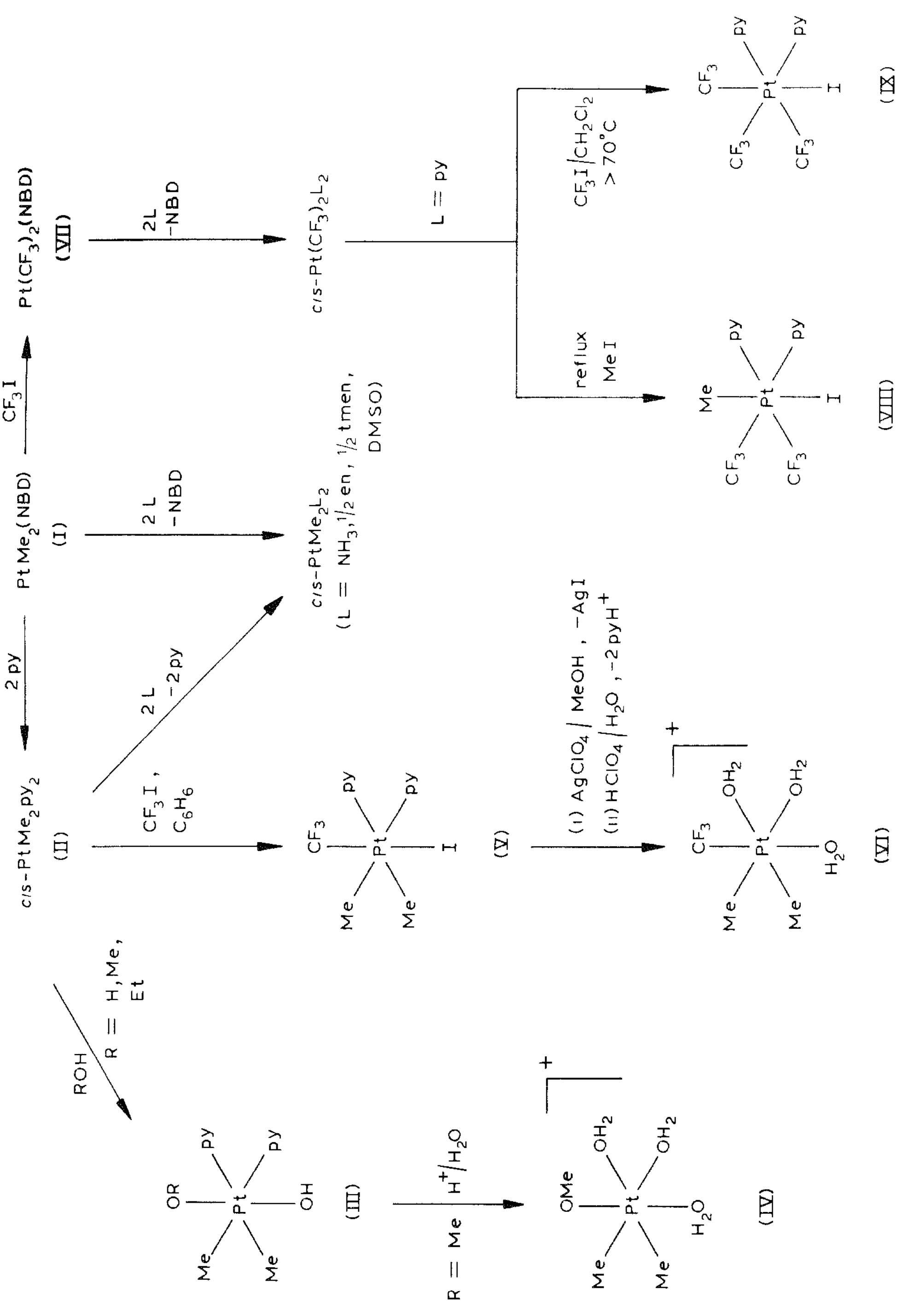

SCHEME 1. Some derivatives of PtMe$_2$(NBD).

careful control of reaction conditions was required to obtain significant yields. I with one mole equivalent of tmen in benzene at 80° C gave $PtMe_2(tmen)$ quantitatively within 45 minutes. This solid is air-stable.

Treatment of I in benzene with ethylenediamine (en) or ammonia gave an immediate white precipitate of $PtMe_2(en)$ or *cis*-$PtMe_2(NH_3)_2$, respectively. The ammine complex is slightly soluble in acetone (^1H NMR, $(CD_3)_2CO$, $\delta(Pt—Me)$ 0.65 ppm, $^2J(Pt—CH_3)$ 81.2 Hz), but $PtMe_2(en)$ is insoluble in common non-coordinating solvents. Both solids slowly decomposed at 25° C, and *cis*-$PtMe_2(NH_3)_2$ decomposed slowly even at 0° C under nitrogen. The low thermal stability of these compounds may be due to involvement of amine hydrogen atoms in intramolecular methane elimination. There was no indication of amine attack on the olefins in these reactions. Dimethylsulfoxide (DMSO) with I in benzene at 25° C gave *cis*-$PtMe_2(DMSO)_2$, which was isolated as a white, air-stable solid, soluble in most organic solvents (except ether) and in water. (^1H NMR, D_2O: $\delta(Pt—Me)$ 0.46 ppm, $^2J(Pt—CH_3)$ 79.1 Hz; $\delta(S—Me)$ 3.01 ppm, $^3J(Pt—S—CH_3)$ 13.7 Hz). Significant $Pt—S—CH_3$ coupling, and $\nu(S{=}O)$ at 1072 and 1095 cm^{-1} in the IR spectrum indicate that DMSO is S-bound, as in *cis*-$PtPh_2(DMSO)_2$ [5]. $PtMe_2(DMSO)_2$ has been previously reported, from *cis*-$PtCl_2(COD)_2$ and $SnMe_4$ in DMSO and characterized by reaction with PPh_3 to give *cis*-$PtMe_2(PPh_3)_2$ [6].

Like $PtMe_2(COD)$ [7], I dissolved in aqueous KCN solution to give *cis*-$K_2[PtMe_2(CN)_2]$. NBD was not displaced from I by MeCN, PhCN, *N,N*-dimethylformamide (DMF), acetylacetonate ($acac^-$), or halide ions.

Pyridine was also easily displaced from *cis*-$PtMe_2py_2$ (II) by DMSO, tmen, en, NH_3, to give the compounds described above. II is also potentially useful in synthesis of new organoplatinum(IV) compounds. Like $PtMe_2(bipy)$ [8], II is extremely reactive toward oxidative addition, adding halogens, MeI, CF_3I, CCl_4, CH_2Cl_2 (but not $CHCl_3$), $PhCH_2Br$, MeCOCl, ICN and PhBr. Like $PtMe_2(bipy)$ [9] it also reacts with water and alcohols, ROH, to give $PtMe_2(OR)(OH)py_2$ (III). Unlike phosphines or bipy, pyridine *trans* to methyl is easily removed by acid from the platinum(IV) products. Examples are given in Scheme 1. *fac*-$PtMe_2(OMe)(H_2O)_3{}^+$ (IV) is, remarkably, stable indefinitely in aqueous acid, with no change in the ^1H NMR spectrum of a dilute D_2SO_4 solution over several weeks ($\delta(Pt—Me)$ 1.05 ppm, $^2J(Pt—CH_3)$ 75.6 Hz, $\delta(OMe)$ 2.43 ppm, $^3J(Pt—O—CH_3)$ 30.1 Hz). V and VI each shows the expected singlet with satellites in its ^{19}F NMR spectrum.

Clark and Manzer [1] noted that COD was more readily displaced from $Pt(CF_3)_2(COD)$ than from $PtMe_2(COD)$, presumably due to the high *trans* effect of trifluoromethyl combined with reduced availability of Pt d_π electrons for back-bonding to the olefin, and reported the facile preparation of a range of compounds *cis*-$Pt(CF_3)_2L_2$, where L = PR_3, AsR_3, ½bipy, ½tmen, and 4-methylpyridine.

$Pt(CF_3)_2(NBD)$ (VII) was prepared in an analogous way to $Pt(CF_3)_2(COD)$ [1], by reaction of $PtMe_2(NBD)$ (I) with CF_3I. NBD was easily displaced by tmen, py, en, NH_3, NCMe, and NCPh, to give compounds *cis*-$Pt(CF_3)_2L_2$ which are stable as solids at 25°C if moisture is excluded. The compounds are all soluble to some extent in acetone, showing the expected singlet with satellites in ^{19}F NMR spectra (e.g., *cis*-$Pt(CF_3)_2(NCPh)_2$ $\delta(F)$ −26.52 ppm from $CFCl_3$, $^2J(Pt—CF_3)$ 864.3 Hz). The spectra of the nitrile complexes in acetone also show two smaller singlets with satellites, ($\delta(F)$ (*trans* to N) —30.06 ppm, $^2J(Pt—CF_3)$ 844.7 Hz; $\delta(F)$ (*trans* to 0) —22.77 ppm, $^2J(Pt—CF_3)$ 937.5 Hz) assigned to *cis*-$Pt(CF_3)_2(NCR)(OCMe_2)$.

From ^{19}F NMR spectroscopy it is clear that NBD is displaced from VII by a number of other donor solvents, although pure solids have not yet been isolated from these solutions. In DMF, one singlet with satellites was observed, with the large $Pt—CF_3$ coupling (883.8 Hz) consistent with a complex, *cis*-$Pt(CF_3)_2$-$(DMF)_2$, with DMF O-bound. With DMSO, two peaks of equal intensity were observed assigned to *cis*-$Pt(CF_3)_2(S(O)Me_2)(OSMe_2)$ (NMR, $CHCl_3$: $\delta(F)$ (*trans* to S) —30.30 ppm; $^2J(Pt—CF_3)$ 788.6 Hz; $\delta(F)$ (*trans* to O) —18.34 ppm, $^2J(Pt—CF_3)$ 881.4 Hz). A much weaker singlet with satellites ($\delta(F)$ —25.24 ppm, $^2J(Pt—CF_3)$ 710.5 Hz) was assigned to *cis*-$Pt(CF_3)_2(S(O)Me_2)_2$. There is no obvious reason why the isomer with mixed coordination modes should be preferred in this case, when only the S-bound isomer is detected for the methyl analogue.

In the presence of added water, ^{19}F peaks due to any of the trifluoromethyl compounds described above slowly decreased in intensity, while a peak due to fluoride ion grew near —162 ppm. Slow decomposition also occurred in methanol, possibly due to traces of water remaining in the solvent.

Trifluoromethyl compounds are much less reactive toward oxidative addition than the corresponding methyl compounds [10], but *cis*-$Pt(CF_3)_2py_2$ did add MeI and CF_3I under forcing conditions (Scheme 1). (IX) is the first reported tris(trifluoromethyl)platinum complex. (NMR, Me_2CO: $\delta(F)$ (*trans* to py) —26.44 ppm, $^2J(Pt—CF_3)$ 424.8 Hz; $\delta(F)$ (*trans* to I) —31.81 ppm, $^2J(Pt—CF_3)$ 390.6 Hz).

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