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Preliminary communication

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^{1}H NMR SPECTRA OF TRIMETHYLPLATINUM(IV) COMPLEXES WITH ETHYLACETOACETATE, METHYLACETOACETATE, DIETHYLMALONATE AND DIMETHYLMALONATE

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Summary

The ^{1}H NMR spectra of the title compounds show that kinetically rigid dimers are present in solution, with metal to γ-carbon bonds, and that the 1/1 adducts of the compounds with pyridine and with 2,2′-bipyridyl contain bidentate and monodentate ester ligands, respectively.

X-ray [1] and neutron diffraction [2] studies on a representative β-diketonate complex of trimethylplatinum(IV) (I:$R^1 = R^2 = n\text{-}C_3H_7$) have shown that it is dimeric in the solid state, with a bridge bond to the γ-carbon atom of the diketone. Molar mass determinations [3] and ^{1}H NMR studies [4] on a range of β-diketonates show that this structure is preserved in solution. Trimethylplatinum(IV) ethylacetoacetate (II:$R^1 = CH_3$, $R^2 = OC_2H_5$) has the centrosymmetric structure in the solid [5], with the R^1 groups *trans*, and is dimeric in freezing benzene [6]. We have found that for complexes II - V, prepared from Me_3PtI and the thallous salt of the ligand in benzene, the dimeric structure is present in solution by molar mass measurement (isopiestically in benzene at 37 °C) and by 100 MHz ^{1}H NMR spectroscopy in $CDCl_3$ and C_6D_6.

The NMR spectra of the complexes, and of their 1/1 adducts with pyridine [$Me_3Pt(R^1COCHCOR^2)py$] (VI) and with 2,2′-bipyridyl [$Me_3Pt(R^1COCHCOR^2)$-bipy] (VII) show the following features.

1. The expected pattern [4] of methyl-platinum resonances is observed at magnet temperature (31 °C). For IV and V, with symmetrical ligands, two signals are seen in the ratio 2/1. For II and III, the two sets of 1/1/1 resonances show the presence of both possible geometrical isomers in solution. Coupling constants $^2J(^{195}Pt—^1H)$ are in the ranges 74.4-78.8 Hz (*trans* to O) and 66.4-71.2 Hz (*trans* to C).

Coalescence of the methyl-platinum resonances at 30 °C in the spectra of

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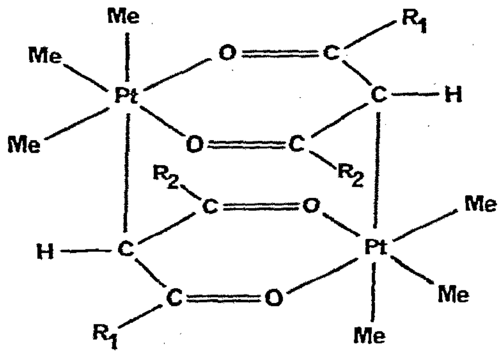

Fig. 1. Structure of β-dicarbonyl complexes of trimethylplatinum(IV) (I:$R^1 = R^2 = n\text{-}C_3H_7$; II:$R^1 = CH_3$, $R^2 = OC_2H_5$; III:$R^1 = CH_3$, $R^2 = OCH_3$; IV:$R^1 = R^2 = OC_2H_5$; V:$R^1 = R^2 = OCH_3$). For $R^1 \neq R^2$ the *trans* isomer is shown. The *cis* isomer has the R^1 and R^2 groups on one of the dicarbonyl ligands interchanged.

the β-diketonates, indicating rapid exchange among the *trans* ligands, is not observed. This is surprising, since the mechanism of exchange involves cleavage of the Pt—C(γ) bond [7], and this bond is longer (256 ± 9 pm) in the ketoester complex II than in the β-diketone complex I (239 ± 3 pm). A further point of contrast is the preservation of the dimer in acetone for IV and V. The spectrum of the acetylacetonate ($R^1 = R^2 = CH_3$) in acetone shows cleavage of the dimer with solvent coordination ($^2J(\text{Pt—CH}_3) = 73.3$ and 82.6 Hz; no coupling to γ-carbon).

2. The coupling constants of the methyl-platinum signals show that the pyridine (VI) and 2,2′-bipyridyl (VII) adducts contain bidentate (O-bonded) and monodentate (C-bonded) ester ligands [J (*trans* to O) = 73.1-77.4 Hz, J (*trans* to C) = 60.9-62.8 Hz, J (*trans* to bipy) = 69.3-70.3 Hz, J (*trans* to py) = 69.7-71.0 Hz]. For the adducts of II and III, three distinct methyl-platinum resonances are seen as each methyl group is in a different environment.

3. In all complexes with OC_2H_5 groups, a complex signal is observed for the non-equivalent CH_2 protons: this appears to be a consequence of hindered rotation.

4. In complexes II-V the γ-carbon proton signal is split by coupling to ^{195}Pt, $^2J = 43.9\text{-}47.0$ Hz, compared to 41.0-42.5 Hz in the β-diketonates [4], while in the bipy adducts VII $J = 53.2\text{-}53.5$ Hz.

An interesting correlation is found in Me_3Pt^{IV} complexes in which one of the methyl-platinum groups is *trans* to a methine CH group. The sum of the respective coupling constants, [$^2J(\text{Pt—CH}_3) + {}^2J(\text{Pt—CH})$] is practically independent of the *cis*-ligands. For nineteen such compounds (this work and ref. 4) a wide variation in both J values, 60.9-75.5 Hz and 41.3-53.5 Hz, respectively, is found, but the sum is 115 ± 1 Hz for all but four compounds. This very specific *trans* effects is being studied.

Acknowledgement

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References

1 A.G. Swallow and M.R. Truter, Proc. Roy. Soc., A, 252 (1960) 205.
2 R.N. Hargreaves and M.R. Truter, J. Chem. Soc., A, (1969) 2282.
3 A.K. Chatterjee, R.C. Menzies, J.R. Steel and F.N. Youdale, J. Chem. Soc., (1958) 1706.
4 J.R. Hall and G.A. Swile, J. Organometal. Chem., 21 (1970) 237; 47 (1973) 195.
5 A.C. Hazell and M.R. Truter, Proc. Roy. Soc., A, 254 (1960) 218.
6 R.C. Menzies and E.R. Wiltshire, J. Chem. Soc., (1933) 21.
7 N.S. Ham, J.R. Hall and G.A. Swile, Aust. J. Chem., 28 (1975) 759.

Book review

Ions and Ion Pairs in Organic Reactions, Vol. 2: Role of Ions and Ion Pairs in Chemical Reactions; edited by M. Szwarc, John Wiley & Sons, New York/London/Sydney/Toronto, 1974, xiii + 566 pages, $28.50, £13.65.

The first volume of this two-volume set was devoted to the study of organic ions and ion pairs by physical methods (review: J. Organometal. Chem. 60 (1973) C46). Except for a chapter on the use of electric permittivity (dielectric constant) in probing the structure and dynamics of ion pairs in solution (E. Grunwald, S. Highsmith, and Ting-Po I), which was intended for volume 1, volume 2 deals with the effects of ion aggregation and solvation on chemical reactivities. Such effects are frequently large; "spectacular" is the word chosen by Szwarc in his preface. Before about 1960, we were ignorant of most of these effects. Today they cannot be ignored.

Three chapters treat mostly systems in which the chemistry of an anion is affected by alkali metal counterions and aprotic solvents (mainly, but not exclusively, ethers). Here the organometallic chemist will find the bulk of the material of interest. The topics are electron transfer reactions of radical anions, carbanions, and solvated electrons (M. Szwarc and J. Jagur-Grodzinski), proton transfer from carbon acids (M. Szwarc, A. Streitwieser, and P.C. Mowery), and ionic polymerization (M. Szwarc). These were chosen because they involve important fundamental reaction steps (electron transfer, proton transfer, and addition of carbanions to carbon—carbon double bonds), because the effects of ion aggregation and solvation are pronounced, and because they have been the subjects of intense recent study.

Another chapter covers solvolytic nucleophilic aliphatic substitution (D.J. Raber, J.M. Harris, and P. v. R. Schleyer), concentrating on the putative dynamic roles of ion pairs. The cornerstones of this area were laid by the late Saul Winstein, to the memory of whom this volume is dedicated.

Of the approximately 1200 citations of literature, about 80% refer to works published in or after 1960, 60% in or after 1965, and 25% in or after 1970. A quick scan revealed only two citations (0.2%) of the Journal of Organometallic Chemistry.

Should a reader of this journal be interested in this book? Not if he hopes to find in it any chemistry of organometallic systems other than ionic organoalkalines. And not if he hopes to find compendia of examples in which