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Preliminary communication

Reactions of some methoxydienylplatinum(II) complexes with carbon monoxide

ALDO VITAGLIANO and GASTONE PAIARO
Istituto Chimico dell'Università, Via Mezzocannone 4, 80134 Napoli (Italy)

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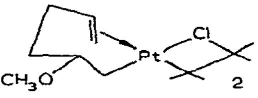
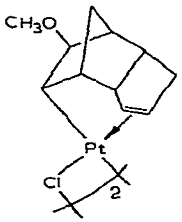
SUMMARY

Carbon monoxide reacts readily with methoxydienylplatinum(II) complexes, but carbonyl insertion into the σ-Pt–C bonds does not occur; instead (chloro)(carbonyl) or (chloro)(methoxycarbonyl) complexes are formed, depending on the nature of the dienyl system.

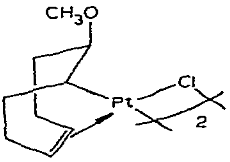
We have examined the reactions of some methoxydienyl complexes of Pt^{II} (Ia)–(IVa) with carbon monoxide and find that carbonyl insertion into the σ C–M bond[1] does not occur, and that the reaction which does take place is strongly dependent on the structure of the organic moiety.



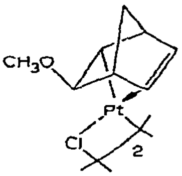
(Ia)



(IIa)

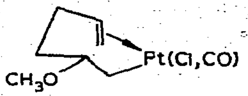


(IIIa)

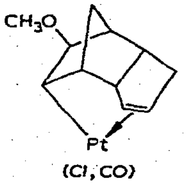


(IVa)

The chloroform solutions of (Ia)–(IVa)[2] absorb CO readily (1 mole of CO per mole of Pt) under mild conditions (atm. press., –20°). The NMR and IR spectra (strong band at 2100 cm^{-1}) of the resulting solutions indicate that monomers of the type (Ib) and (IIb) are formed from (Ia) and (IIa), respectively. Species (Ib) and (IIb) are in equilibrium with the starting dimers which are re-formed on removal of the solvent. (Ib) and (IIb) are stable for several days at low temperature in chloroform saturated with CO, but decompose above 0° to give metallic platinum, the precursor diene π-complexes, and unidentified organic compounds.



(Ib)



(IIb)

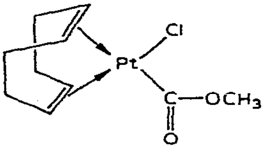
Treatment of (IIIa) with CO yields a crystalline solid (white needles, recrystallized from benzene/heptane) with the spectral properties shown in Table 1. From these structure (IIIb) can be assigned. The strong IR absorption at 1665 cm^{-1} can be assigned to CO stretching[3a]. The NMR peaks at δ 5.82 and δ 5.04 can be assigned to the four olefinic protons of the cyclooctadiene. In the mass spectrum the parent peak indicates a molecular weight of 396 (based on ^{194}Pt and ^{35}Cl). The formation of compound (IIIb) is a two step process which can be followed by IR and NMR methods. First the CO reacts rapidly, with splitting of the chlorine bridges, as in the cases of (Ib) and (IIb). The second, slower, step involves migration of the methoxyl group to the coordinated CO group, and isotopic exchange with CD_3OD in chloroform solution suggests a dissociative mechanism for this. NMR evidence shows that the rate of exchange of the methoxyl group of species A with CD_3OD decreases in the order: (I) >> (III) >> (II).

TABLE 1

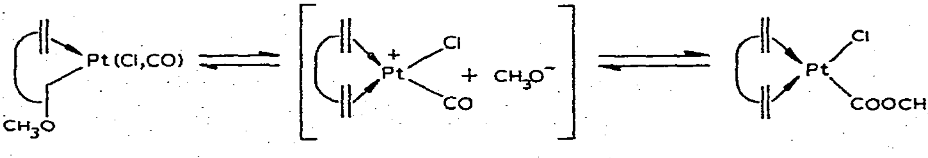
SELECTED DATA FROM THE IR, NMR AND MASS SPECTRA OF $C_8H_{12}PtClCOOCH_3$ (IIIb)

IR (Nujol mull) (cm^{-1})	1665 s, 1075 s (broad)
NMR ($CDCl_3$) δ	5.82(2H,bs), 5.04(2H,bs)[a], 3.68(OCH_3,s)[a], 2.46(8H,bm)
Mass Sp. (*m/e*)[b]	396(M^+), 365(M^+-OCH_3), 337($M^+-COOCH_3$), 59($COOCH_3^+$)

[a] Two ^{135}Pt satellite peaks are observable (^2J(H–Pt) 35 Hz, ^2J(H–Pt) 76 Hz and ^4J(H–Pt) 6 Hz respectively).
[b] Based on ^{194}Pt and ^{35}Cl isotopes.



(IIIb)



(A) (B)

Nucleophilic attack of alkoxide ion on a coordinated CO in Pt^{II} cationic complexes is a known reaction[3]. However, as far as we know, an intramolecular migration of the type suggested above has not previously been observed.

Reaction of (IVa) with CO yields a crystalline solid (white needles, recrystallized from benzene/heptane). Its spectroscopic characteristics, shown in Table 2, indicate structure (IVb). The IR absorption at 2080 cm^{-1} is assigned to the terminal CO stretching.

TABLE 2

SELECTED DATA FROM THE IR, NMR AND MASS SPECTRA OF $(C_7H_8OCH_3PtClCO)_2$ (IVb)

IR (Nujol mull) (cm^{-1}) 3070 w, 2080 s, 1110 s, 825, 810 m
NMR ($CDCl_3$) δ 4.08(1H,bs), 3.36(OCH_3,s), 2.58(1H,bs)[a], 2.24(1H,bs)[a] 1.70 1.20(5H,m)
Mass Sp. (*m/e*)[b] 760(M^+), 732(M^+–CO), 704(M^+–2CO), 123($C_7H_8OCH_3^+$)

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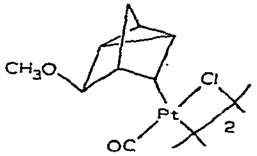
[a] Two ^{195}Pt satellite peaks are observable (*J* 113 Hz and *J* 17 Hz respectively).
[b] Based on ^{194}Pt and ^{35}Cl isotopes.

The band at 3070 and the doublet centered at 817 cm^{-1} are characteristic of a nortricyclene substituted ring[4]. The NMR spectrum does not show olefinic protons. The parent peak in the mass spectrum gives a molecular weight of 760 (based on ^{194}Pt and ^{35}Cl).

Reactions of the type (IVa) → (IVb), in which a nortricyclene ring system is formed are known to be induced by ligands other than CO[5]. The special electronic structure of (IVa), which can be represented as a π-homoallylic system[6], accounts for this behaviour. The different behaviour of the electronically similar compounds (I), (II) and (III) in the reaction A → B thus appears somewhat anomalous, since the methoxyl group exchange which occurs in chloroform solution of A should in principle make possible methoxyl migration to the CO group in all three cases. Our results suggest that in the systems studied the difference of "electrophilicity" between the coordinated olefin and the coordinated CO group must be rather small, since a modification of the hydrocarbon moiety suffices to change the site of the methoxide ion attack.



(IVb)

ACKNOWLEDGEMENT

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