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Preliminary communication

CHELATING MONOOLEFIN—ANILINE COMPLEXES OF PLATINUM(II)

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Summary

Bidentate ligands containing an olefin and an aniline, or *N*-substituted aniline, nitrogen donor have been synthesized, and platinum(II) chelates prepared from them.

Platinum(II) complexes of chelating olefin—Group V ligands have been the subject of extensive investigation [1-3]. The coordinated olefinic group in these compounds reacts with various nucleophiles and electrophiles to give stable platinum chelates containing metal—carbon σ bonds. These have been suggested to provide models for the more transient intermediates formed in metal-catalysed olefin reactions [1, 3].

The bond between the metal and a heavy Group V donor atom is thought to rely, in part, upon the π-acceptor ability of the latter [4], which implies a sharing of the metal d_π electrons between the Group V donor and the olefin. Subsequent reaction of the olefin may then be influenced to an unknown extent by the π-acceptor properties of the Group V element. In view of this it seemed desirable to extend the series of *o*-substituted phenyl monoolefins to include various amine groups, the donor nitrogen of which makes no demands upon the d_π electrons of the metal [5].

We report herein the isolation of the first of these chelate complexes of platinum(II) (I) for the following olefin—*o*-phenylamine ligands; *o*-vinylaniline (VHN), *N*,*N*-dimethyl-*o*-vinylaniline (VMN), *o*-isopropenylaniline (IHN) and *N*,*N*-dimethyl-*o*-isopropenylaniline (IMN)*. The complexes Pt(VHN)Cl_2 and Pt(IHN)Cl_2 are the first *o*-phenylmonoolefin chelates to be reported in which the Group V donor is unsubstituted.

As with analogous coordinated olefins [1, 2] the infrared absorption attributed to the stretching vibration of the olefinic double bond (ν(C=C)) of the free ligand is shifted and although not observed, presumably occurs as a

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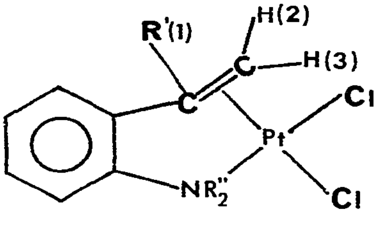
*Satisfactory analyses have been obtained for the ligands and complexes.

TABLE 1

100 MHz ^{1}H NMR DATA FOR OLEFIN—AMINES AND THEIR Pt^{II} COMPLEXES

Compounds	Vinyl protons									Amine protons	
	Chemical shift [a]			Coupling constants [b]						Chemical shift [a]	Coupling constants [b]
	δ1	δ2	δ3	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	J(Pt-1)	J(Pt-2)	J(Pt-3)	δ	^3J(Pt—N—C—H)
VHN	6.97	5.24	5.58	11.0	17.2	1.8	-	-	-	[c]	-
Pt(VHN)Cl$_2$	5.74	4.91	4.30	7.8	12.8	0.8	58.0	67.3	68.5	[c]	-
Δδ[f]	−1.23	−0.33	−1.28	-	-	-	-	-	-	-	-
VMN	7.05	5.24	5.72	11.4	17.7	1.7	-	-	-	2.68	-
Pt(VMN)Cl$_2$	5.64	5.16	4.38	7.7	12.7	0.8	53.5	68.8	72.8	3.44, 3.42[d]	29.1, 31.2
Δδ	−1.41	−0.08	−1.24	-	-	-	-	-	-	+0.76, +0.74	-
IHN	2.05	5.04	5.27	1.0	1.6	2.3	-	-	-	[c]	-
Pt(IHN)Cl$_2$	2.14	4.84	4.24	0.4	[e]	0.8	38.1	69.5	72.8	[c]	-
Δδ	+0.09	−0.20	−1.03	-	-	-	-	-	-	-	-
IMN	2.13	5.06	5.06	1.2	1.2	[e]	-	-	-	2.71	-
Pt(IMN)Cl$_2$	2.24	5.03	4.30	0.5	0.2	0.7	33.0	70.1	75.7	3.47, 3.45[d]	29.7, 32.0
Δδ	+0.11	−0.03	−0.76	-	-	-	-	-	-	+0.76, +0.74	-

[a] Measured in ppm from TMS as internal standard. Solvent; dimethylformamide-d_7. [b] Measured in Hz. [c] See text. [d] N—CH$_3$ groups become non-equivalent on coordination to the platinum. [e] Not observed. [f] Δδ = ligand proton shift on coordination. Downfield shifts are denoted as positive.



[I]

Ligand	R′	R″
VHN	H	H
VMN	H	CH_3
IHN	CH_3	H
IMN	CH_3	CH_3

weak band obscured by other ligand vibrations in the region 1485-1500 cm^{-1}.

In the primary amine complexes $Pt(VHN)Cl_2$ and $Pt(IHN)Cl_2$ the N—H stretching frequencies have dropped well below the free ligand values (ca. 230 and 320 cm^{-1} respectively) as might be expected when the nitrogen is coordinated to the metal [6].

The ^1H NMR spectra of the complexes show an upfield shift of the vinylic protons, H(2) and H(3) (and H(1) in the VHN and VMN complexes) and a decrease in the coupling constants $J_{1,2}$, $J_{2,3}$ and $J_{1,3}$ relative to the corresponding free ligands. These coordination shifts are similar to those found for other aromatic monoolefin complexes [7,8] and together with the observation of $^{195}Pt—^1H$ (olefin) coupling (Table 1) provide further evidence for platinum—olefin bonding. Coordination of the nitrogen atom in the complexes $Pt(VMN)Cl_2$ and $Pt(IMN)Cl_2$ is confirmed by a downfield shift of the R″ protons and by appearance of $^{195}Pt—^1H(CH_3)$ coupling (^3J(Pt—N—C—H)) (Table 1). The ^1H resonances of the amine protons in the ligands VHN and IHN and their platinum complexes are broad and have yet to be unequivocally assigned.

Complexes and reactions similar to those exhibited by other chelating monoolefins [3] may be envisaged. This is supported by our preliminary investigation of the reactions of the platinum(II)—olefin—amine chelates.

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