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A ^{1}H NMR STUDY OF THE BONDING IN OLEFIN—PLATINUM COMPLEXES CONTAINING PHENOLATO AND THIOPHENOLATO LIGANDS: EVIDENCE FOR M→S π-BONDING

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Summary

Two series of olefin—platinum(II) complexes, one containing a phenolato and the other a thiophenolato ligand *trans* to the olefin, have been prepared. The ^{195}Pt—^{1}H (olefin) coupling constants have been used in conjunction with the pK_a of the *trans* ligands to reveal a significant degree of π-acid character in the thiophenolato-sulphur atom.

Introduction

In a previous paper [1] we suggested that the coupling between the ^{195}Pt nucleus and the olefinic protons in chelating monoolefin—anilineplatinum(II) complexes may be used as a sensitive probe for assessing the π-acid character of the ligand *trans* to the olefin. We have now prepared two series of isostructural olefin—platinum complexes of the type Pt(IMN)ClL (Fig. 1). In one of these a phenolato ligand lies *trans* to the olefin while in the other a thiophenolato group occupies this position.

By varying the substituents on the phenolato and thiophenolato rings we have provided a range of basicity at the oxygen or sulphur donor atom. The

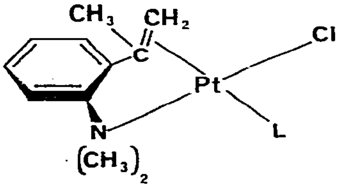


Fig. 1. Structure of the complexes Pt(IMN)ClL.

resulting changes in J(Pt—C—H(olefin)) are discussed with reference to the bonding between the platinum atom and the Group VI donor.

Experimental

o-Isopropenyl-*N*,*N*-dimethylaniline (IMN) was prepared by methylation [2] of the amine groups of *o*-isopropenylaniline [3]. The thallium(I) derivatives of the phenols and thiophenols were made by reaction of thallium(I) ethoxide with the appropriate phenol or thiophenol [4].

Pt(IMN)Cl_2, dichloro-*o*-isopropenyl-*N*,*N*-dimethylanilineplatinum(II), was synthesized from Zeise's salt using the method previously described [1] for Pt(VMN)Cl_2 (VMN = *o*-vinyl-*N*,*N*-dimethylaniline). Found: C, 30.99; H, 3.44; N, 3.21; Cl, 16.9%. $C_{11}H_{15}NCl_2Pt$ calcd.: C, 30.92; H, 3.54; N, 3.28; Cl, 16.6%.

Infrared absorptions at 340(s) and 307(m) cm^{-1} are attributed to the platinum—chlorine stretching vibrations.

TABLE 1

ANALYTICAL, INFRARED AND MELTING POINT DATA FOR THE COMPLEXES Pt(IMN)ClL

HL	Analysis (Found (calcd.) (%))					(Pt-Cl)	Melting point (°C)
	C	H	N	Cl	S		
Phenol	41.78 (42.11)	4.37 (4.16)	2.90 (2.89)	7.3 (7.3)	—	349	137d
4-Chlorophenol	39.73 (39.31)	3.70 (3.69)	2.56 (2.70)	14.2 (13.7)	—	340	135d
3,5-Dichlorophenol	36.44 (36.87)	3.38 (3.28)	2.84 (2.53)	19.3 (19.2)	—	348	165—168d
3-Nitrophenol	38.10 (38.53)	3.78 (3.43)	5.09 (5.29)	7.3 (6.7)	—	348	172—174d
4-Hydroxybenzaldehyde	41.80 (42.15)	4.14 (3.93)	2.55 (2.73)	7.0 (6.9)	—	339	135—138d
4-Nitrophenol	38.34 (38.53)	3.55 (3.61)	5.17 (5.29)	6.8 (6.7)	—	343	178—182d
2,6-Dichlorophenol	36.61 (36.87)	3.27 (3.28)	2.57 (2.53)	19.4 (19.2)	—	347	169—171d
Pentafluorophenol	35.49 (35.52)	2.77 (2.63)	2.66 (2.44)	6.5 (6.2)	—	350	158—160d
Pentachlorophenol	30.89 (31.07)	2.29 (2.30)	2.16 (2.13)	32.5 (32.4)	—	349	181—184d
2,4-Dinitrophenol	35.35 (35.52)	3.18 (3.16)	7.13 (7.31)	6.0 (6.2)	—	340	183—187d
3-Methylthiophenol	41.91 (41.98)	4.22 (4.31)	2.70 (2.72)	7.0 (6.9)	6.1 (6.2)	343	226d
4-Methylthiophenol	40.26 (41.98)	4.02 (4.31)	2.94 (2.72)	9.0 (6.9)	6.0 (6.2)	344	223d
Thiophenol	40.22 (40.76)	3.94 (4.02)	2.69 (2.80)	7.5 (7.1)	5.9 (6.4)	343	210d
4-Chlorothiophenol	37.95 (38.14)	3.57 (3.58)	2.46 (2.62)	13.5 (13.2)	5.4 (6.0)	341	253d
4-Nitrothiophenol	37.12 (37.40)	3.65 (3.51)	4.85 (5.13)	6.9 (6.5)	5.6 (5.9)	334	237d
Pentafluorothiophenol	34.37 (34.55)	2.53 (2.56)	2.54 (2.37)	6.9 (6.0)	5.4 (5.4)	339	187d
Pentachlorothiophenol	29.92 (30.33)	2.14 (2.25)	1.85 (2.08)	32.3 (31.6)	4.3 (4.8)	337	221d

The phenolato and thiophenolato complexes were also prepared by the previously described method [1]. Analytical, infrared and melting point data for these compounds are given in Table 1.

The ^{1}H NMR spectra of IMN and its platinum(II) complexes were recorded on a Varian HA 100, 100 MHz spectrometer using DMF-d_7 solutions with TMS as internal standard.

Infrared spectra of the complexes were run on a Perkin—Elmer PE 457 grating infrared spectrophotometer calibrated with polystyrene film. The frequencies recorded are believed to be accurate to ±2 cm^{-1}.

Melting points were measured in air on a Reichert hot-stage melting point apparatus with microscope and are corrected.

Microanalyses were performed by the Australian Microanalytical Service, Division of Applied Organic Chemistry, C.S.I.R.O., University of Melbourne.

Results and discussion

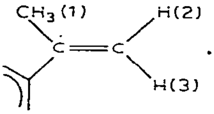
The investigation reported in this paper originated in an attempt to assess, through changes in allylic coupling [5], the extent of the interaction of the π-bonds ($2p\pi$, $2p\pi^*$) of the olefin with the atomic orbitals of the platinum. It was assumed that by altering the nature of the ligand *trans* to the olefin the degree of π-character in the carbon—carbon bond of the olefin would vary. Since allylic coupling is allegedly [6] transmitted primarily through the π-system of the olefin it was expected that a correlation might exist between the allylic coupling constants and the π-acid character of the *trans* ligand. In fact, as Table 2 shows, π-allylic coupling was reduced, on coordination of the olefin, to a negligible level and was thus quite insensitive to the nature of the *trans* donor group.

TABLE 2

INTERPROTON COUPLING CONSTANTS (Hz)[a] FOR COMPLEXES OF THE TYPE Pt(IMN)ClL

HL	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
Phenol	0.4	0.2	*b*
4-Nitrophenol	0.5	0.1	*b*
2,6-Dichlorophenol	0.4	0.4	*b*
Pentafluorophenol	0.4	0.1	*b*
Pentachlorophenol	0.4	*b*	*b*
2,4-Dinitrophenol	0.6	<0.1	0.7
3-Methylthiophenol	0.4	0.1	*b*
Thiophenol	0.4	0.1	0.9
4-Chlorothiophenol	0.4	0.1	0.8
4-Nitrothiophenol	0.5	0.1	0.6
Pentafluorothiophenol	0.4	<0.1	0.7
Pentachlorothiophenol	0.5	0.1	0.3

[a] Proton numbering scheme



. [b] Not measurable.

TABLE 3

^{195}Pt—^{1}H COUPLING CONSTANTS (Hz) AND CHEMICAL SHIFTS (δ (ppm) in parentheses) FOR COMPLEXES OF THE TYPE Pt(IMN)ClL

HL	pK_a	J(Pt(1))	J(Pt(2))	J(Pt(3))
Phenol	10.00	29.0(2.24)	64.9(4.64)	69.5(3.99)
4-Chlorophenol	9.38	30.6(2.25)	65.2(4.68)	70.2(4.03)
3-Nitrophenol	8.40	32.0(2.29)	66.5(4.77)	72.0(4.14)
3,5-Dichlorophenol	8.25	32.1(2.29)	67.4(4.78)	72.0(4.15)
4-Hydroxybenzaldehyde	7.62	32.0(2.30)	67.7(4.80)	72.1(4.17)
4-Nitrophenol	7.15	33.1(2.31)	68.4(4.85)	72.9(4.22)
2,6-Dichlorophenol	6.72	32.9(2.17)	68.7(4.63)	74.0(3.91)
Pentafluorophenol	5.53	34.0(2.20)	71.5(4.77)	75.7(4.11)
Pentachlorophenol	4.74	35.0(2.18)	72.4(4.72)	75.8(4.04)
2,4-Dinitrophenol	4.11	35.2(2.28)	72.5(4.88)	77.0(4.28)
3-Methylthiophenol	6.58	23.0(2.23)	56.6(4.88)	63.0(4.33)
4-Methylthiophenol	6.52	22.9(2.23)	56.8(4.85)	62.7(4.32)
Thiophenol	6.43	23.0(2.24)	57.7(4.88)	63.0(4.33)
4-Chlorothiophenol	5.90	23.6(2.27)	58.9(4.91)	64.4(4.38)
4-Nitrothiophenol	4.50	23.8(2.38)	58.7(5.07)	64.7(4.61)
Pentafluorothiophenol	2.68	25.9(2.23)	60.6(4.97)	67.3(4.44)
Pentachlorothiophenol	2.26	25.9(2.22)	60.2(4.92)	67.0(4.38)

On the other hand, it has been authoritatively stated [7—9] that the coupling of ^{195}Pt to other nuclei of spin $\frac{1}{2}$ depends on the overlap and occupancy of orbitals involving the 6s atomic orbital of platinum. If this is so, such coupling provides a probe into the σ-component of the platinum—olefin bond. Since π-acceptance and therefore σ-donation, by the olefin would, in the Dewar—Chatt—Duncanson scheme of olefin bonding [10], be influenced by the π-acidity of the *trans* ligand, it was reasoned that the π-acidity of the latter ligand would be reflected by J(Pt—C—H(olefin)).

An important feature of the compounds studied is that any change in the π-interaction due to the *trans* ligand is confined to a single π-acid ligand (the olefin group). This is in contrast to many other systems where the effect of small variations in the π-acidity of a given type of ligand is diluted by the presence of more than one of the π-acceptor ligands in which the effect is being observed (e.g infrared studies of substituted metal carbonyl complexes [11]).

The following argument assumes that the oxygen donor of the phenolato ligands is incapable of π-acceptance so that variations arising on changing the substituents on the phenyl rings are transmitted to the platinum by σ-bonding alone.

The changes in pK_a * of the phenolato ligands as the electron-donating-

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* There are probably better indicators of the σ-donor ability of the *trans* ligand than pK_a e.g. gas phase proton affinity or ionization potential. A lack of such data for the phenolato and thiophenolato ligands has restricted us to the use of pK_a, a free energy function which embraces in this case an unwanted entropy term.

The enthalpy change, ΔH(HL), in the formation of proton complexes is alleged [12] to reflect the difference in σ-electron density on the donor atoms while the entropy changes which accompany the association of protons with anions are roughly equal. To verify the latter assumption Barnett [13] examined the thermodynamic data for a wide range of anions, using literature values obtained under the same experimental conditions [14]. The variation of ΔS(HL) was found to be ±6 e.u. about a mean value of 26 e.u. This range of ±6 e.u. is equivalent to ±1.3 pK_a units which is not a sufficient variation to affect our arguments based on the use of pK_a.

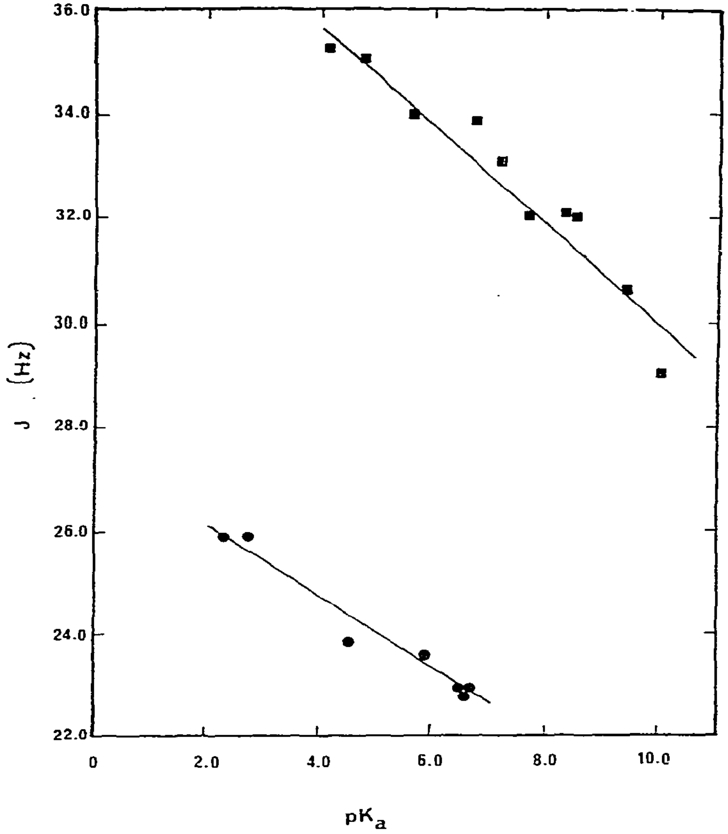

Fig. 2. Variation of $J(^{195}Pt—^1H(1))$ with the pK_a of HL in complexes of the type Pt(IMN)ClL.

	O-donors (■)	S-donors (●)
Slope	—1.0 ± 0.2	—0.7 ± 0.1
Intercept	39 ± 1	28 ± 1
Correlation coefficient	0.97	0.98

withdrawing groups are varied is shown in Table 3. As the ligands become more basic there is a greater transfer of σ-electron density to the platinum, and this is reflected in a lower value of J(Pt—C—H(olefin)). That is, build up of electron density on the metal discourages σ-donation from the olefin and hence lowers the coupling constant. This trend is shown on plotting pK_a (phenolato) vs. J(Pt—C—H(olefin)) (Fig. 2—4).

If a sulphur atom, with empty, low-lying 3*d* orbitals, is now substituted for the oxygen donor a series of isostructural * thiophenolato complexes is obtained (Table 3). The plots of pK_a (thiophenolato) vs. J(Pt—C—H(olefin)) (Fig. 2—4) for this series of compounds also show a linear relationship, but differ

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* Evidence to suggest that the phenolato and thiophenolato complexes are isostructural in their coordination geometry is provided by the single γ(Pt—Cl), the similarity of the ^1H NMR spectra (Table 3) and our previous structural analyses of the compounds $Pt(VMN)Cl(OC_6F_5)$ and $Pt(VMN)Cl(SC_6F_5)$ [1].

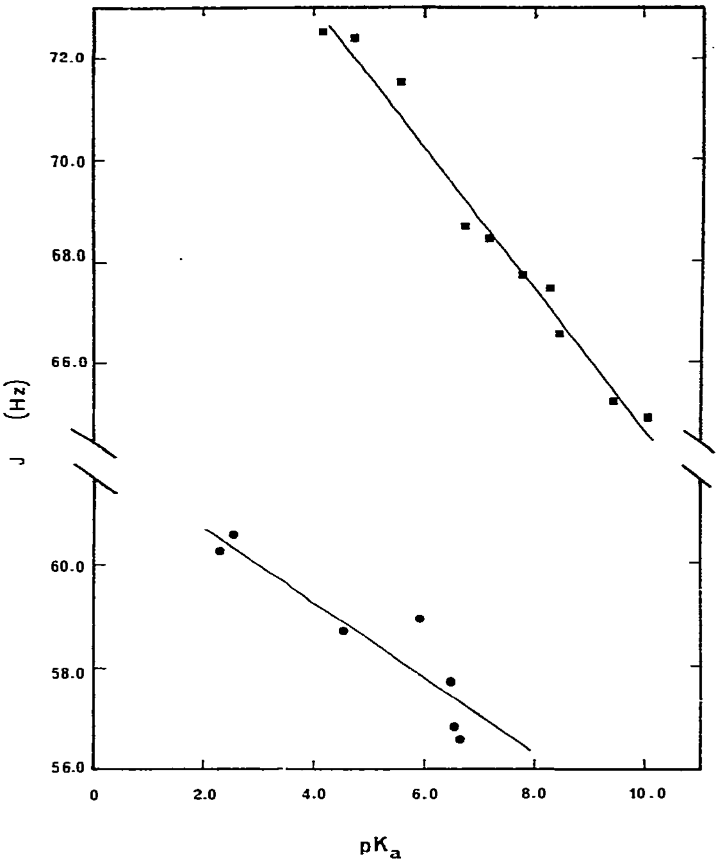

Fig. 3. Variation of $J(^{195}Pt-^{1}H(2))$ with the pK_a of HL in complexes of the type Pt(IMN)ClL.

	O-donors (■)	S-donors (●)
Slope	—1.4 ± 0.2	—0.8 ± 0.4
Intercept	79 ± 1	62 ± 2
Correlation coefficient	0.99	0.92

from those of the phenolato series in that they have a lower (absolute) slope.

As might be expected, towards lower basicity the influence of both types of *trans* ligand on *J*(Pt—C—H(olefin)) is diminished and therefore *J*(Pt—C—H-(olefin)) increases.

It is significant that in Fig. 2—4 the *J*(Pt—C—H(olefin)) values for the thiophenolato complexes lie under those for the phenolato compounds. Since the pK_a of any thiophenolato ligand is lower than its phenolato counterpart it might have been expected, from a consideration of σ-bonding alone, that the thiophenolato plots would lie above those of the phenolato complexes.

The fact that they can not be rationalized on the basis of a degree of $d\pi \rightarrow d\pi$ interaction between the metal and the sulphur. This would lead to competition with the π^* orbitals of the olefin for metal π-electron density and would, by synergism, reduce the σ-donation from the olefin, and hence lower *J*(Pt—C—

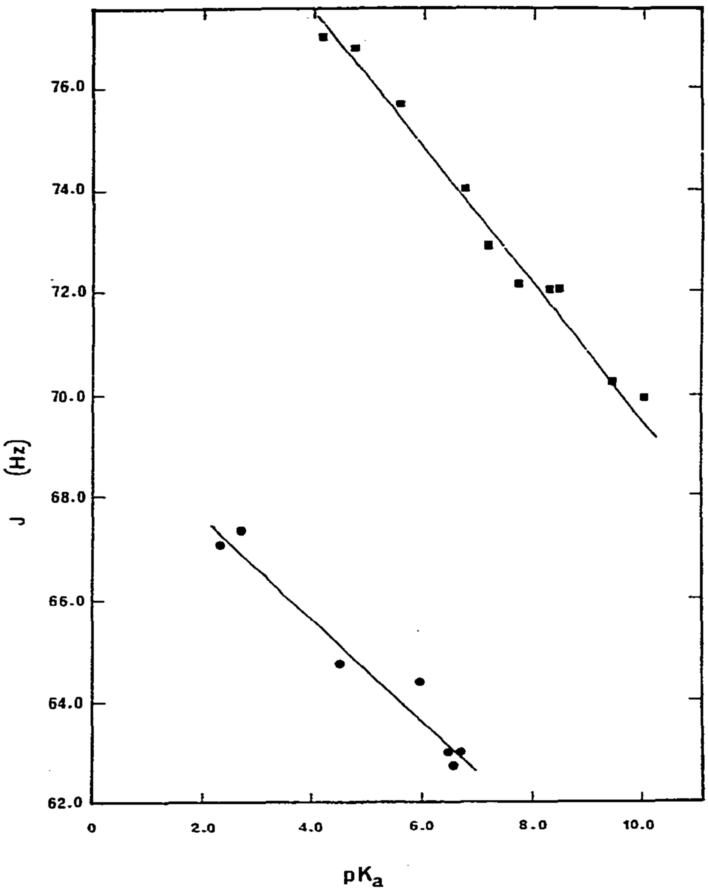

Fig. 4. Variation of $J(^{195}Pt—^{1}H(3))$ with the pK_a of HL in complexes of the type Pt(IMN)ClL.

	O-donors (■)	S-donors (●)
Slope	—1.3 ± 0.1	—1.0 ± 0.3
Intercept	83 ± 1	70 ± 1
Correlation coefficient	0.99	0.98

H(olefin)) in the thiophenolato series.

It is also apparent that for each olefinic proton the lines for the phenolato and thiophenolato complexes converge towards higher pK_a values (Fig. 2—4). As the pK_a of the thiophenolato ligands increases so does the electron density on the sulphur, making it increasingly unattractive to the π-electrons of the platinum. The π-acceptor ability of the sulphur therefore decreases with increasing pK_a and it approaches oxygen in character in that at higher pK_a values bonding between the platinum and sulphur tends towards a purely σ interaction.

There is no indication from this work of the absolute degree of π-acidity of the thiophenolato sulphur atom. Both the formal 2+ charge on the platinum and the negative charge on the thiophenolato ligands militate against π-back bonding. However it seems from the trends in $J(\mathrm{Pt{-}C{-}H(olefin)})$, that the sulphur atom of the thiophenolato ligands has some degree of π-acidity.

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