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## Complexes of the Platinum Metals. 18.<sup>1</sup> Coordination and Fragmentation of *p*-Tolyl Isocyanate

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*p*-Tolyl isocyanate (RNCO) undergoes coordination and fragmentation reactions with  $[\text{MHX}(\text{CO})(\text{PPh}_3)_3]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ),  $[\text{MH}_2(\text{CO})(\text{PPh}_3)_3]$ , and  $[\text{RuH}_2(\text{PPh}_3)_4]$  or  $[\text{OsH}_4(\text{PPh}_3)_3]$  to yield products containing formamide ( $\text{RN}=\text{CH}=\text{O}$ ), ureylene  $\{\text{RN}-\text{C}(\text{O})-\text{NR}\}$ , and formamidinate ( $\text{RN}=\text{CH}=\text{NR}$ ) ligands, respectively. The new complexes  $[\text{MX}(\text{RN}=\text{CH}=\text{O})(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{MH}(\text{RN}=\text{CH}=\text{O})(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{M}\{\text{RN}-\text{C}(\text{O})-\text{NR}\}(\text{CO})_2(\text{PPh}_3)_2]$ , and  $[\text{MH}(\text{RN}=\text{CH}=\text{NR})(\text{CO})(\text{PPh}_3)_2]$  have been characterized by analytical and spectroscopic methods.

### Introduction

As part of an ongoing study of the coordination chemistry of heteroallenes, we have previously reported on the reactions of carbon disulfide,<sup>2</sup> organic isothiocyanates<sup>3</sup> and organic carbodiimides<sup>4,5</sup> with a selection of platinum metal-hydrido complexes. We now report on the logical extension of our investigation to organic isocyanates and describe new products obtained by the coordination and fragmentation of the isocyanate (RNCO) moiety. A preliminary account of this work has previously been published.<sup>6</sup> The reactions of organic isocyanates with transition-metal complexes have recently been reviewed.<sup>7</sup>

### Experimental Section

Hydrido complexes were prepared as previously described<sup>8</sup> by using platinum metal salts supplied by Johnson Matthey and Co. Ltd. *N-p*-Tolyl isocyanate was obtained from Aldrich Chemical Co. Ltd. and was used as purchased. Reagent grade organic solvents were dried over molecular sieves and degassed before use. The petroleum ether used had a boiling range of 60–80 °C. Reactions were performed under a nitrogen atmosphere, but products were worked up in air. Analyses, by the microanalytical laboratory of University College, London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. Proton and phosphorus-31 NMR spectra were obtained at 90 and 36.43 MHz, respectively, with a Bruker HFX90 NMR spectrometer. Infrared spectra were run as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Spectroscopic data are recorded in Table II.

**Carbonylchloro(*N-p*-tolylformamido)bis(triphenylphosphine)ruthenium(II).** A mixture of *p*-tolyl isocyanate (0.2 mL) and carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.34 g) in toluene (20 mL) was heated under reflux for 6 h. The resultant dark yellow-brown solution was allowed to cool to ambient temperature, filtered, and then concentrated to an oil under reduced pressure. The oil was dissolved in the minimum volume of dichloromethane and then diluted with methanol (10 mL) to precipitate the required product as a pale yellow solid. The precipitate was filtered off, washed successively with methanol and petroleum ether, and recrystallized from dichloromethane-methanol to yield pale yellow microcrystals (0.17 g, 59%).

**Bromocarbonyl(*N-p*-tolylformamido)bis(triphenylphosphine)ruthenium(II)** was similarly prepared from *p*-tolyl isocyanate and bromocarbonylhydridotris(triphenylphosphine)ruthenium and was purified and crystallized as described above to yield yellow microcrystals (60%).

**Carbonylhydrido(*N-p*-tolylformamido)bis(triphenylphosphine)ruthenium(II)-Dichloromethane (4/1).** A mixture of *p*-tolyl isocyanate (0.2 mL) and carbonyldihydridotris(triphenylphosphine)ruthenium (0.4 g) in benzene (20 mL) was heated under reflux for 15 min. The clear orange-yellow solution was cooled to ambient temperature, filtered, and then concentrated to an oil under reduced pressure. The oil was dissolved in the minimum volume of dichloromethane and then diluted with methanol (10 mL) to precipitate the required product as a light grey solid. The precipitate was filtered off, washed successively with methanol and petroleum ether, and then recrystallized from dichloromethane-methanol to yield the dichloromethane solvated product as white microcrystals (0.16 g, 47%).

**Carbonylhydrido(*N-p*-tolylformamido)bis(triphenylphosphine)osmium(II).** A mixture of *p*-tolyl isocyanate (0.4 mL) and carbonyl-

dihydridotris(triphenylphosphine)osmium (0.9 g) in toluene was heated under reflux for ca. 7<sup>1</sup>/<sub>2</sub> h. The clear pale yellow solution was cooled to ambient temperature, filtered and then concentrated to an oil under reduced pressure. The oil was dissolved in the minimum volume of dichloromethane and then diluted with methanol (10 mL) to give a grey solid (0.29 g). This grey product, which was contaminated by starting material, was washed successively with methanol and petroleum ether. The filtrate from the above product was again concentrated under reduced pressure and crystallized from methanol to give a white solid, which was free from the starting material. This was recrystallized from dichloromethane-methanol to yield the pure product as white microcrystals (0.38 g, 43%).

**Dicarbonyl(ureylene)bis(triphenylphosphine)ruthenium(II).** Carbonyldihydridotris(triphenylphosphine)ruthenium (0.4 g) and *p*-tolyl isocyanate (0.3 mL) in toluene (20 mL) were heated under reflux for 5 h. The clear reddish brown solution was cooled to ambient temperature, filtered, and then concentrated to an oil under reduced pressure. The oil was dissolved in the minimum volume of dichloromethane and the solution was then diluted with methanol (10 mL) to give an orange-yellow solid. This was filtered off and washed successively with methanol and petroleum ether and then recrystallized from dichloromethane-methanol to yield orange crystals (0.18 g, 45%).

**Dicarbonyl(ureylene)bis(triphenylphosphine)osmium(II)** was similarly prepared from *p*-tolyl isocyanate (0.3 mL) and carbonyldihydridotris(triphenylphosphine)osmium (0.4 g) in toluene (20 mL) and was purified and crystallized as described above to yield microcrystals (0.21 g, 52%).

**Carbonylhydrido(*N,N'*-di-*p*-tolylformamidinato)bis(triphenylphosphine)ruthenium(II)-Methanol (1/1).** A mixture of *p*-tolyl isocyanate (0.3 mL) and dihydridotetrakis(triphenylphosphine)ruthenium (0.6 g) in benzene (20 mL) was heated under reflux for ca. 30 min. The dark yellow-brown solution was concentrated to an oil under reduced pressure. The oil was dissolved in dichloromethane (10 mL) and then passed through an alumina column to remove impurities. The clear yellow-brown solution collected off the column was concentrated under reduced pressure and then diluted with methanol (10 mL) to give a pale yellow solid. This was filtered off, washed successively with methanol and petroleum ether, and then recrystallized from dichloromethane-methanol to give the methanol-solvated product as pale yellow microcrystals (0.24 g, 53%).

**Carbonylhydrido(*N,N'*-di-*p*-tolylformamidinato)bis(triphenylphosphine)osmium(II)** was similarly prepared from *p*-tolyl isocyanate (0.3 mL) and tetrahydridotris(triphenylphosphine)osmium (0.6 g) in benzene (20 mL) and was purified and crystallized as described above to yield pale yellow microcrystals (0.26 g, 56%).

### Results and Discussion

$[\text{MX}(\text{RN}=\text{CH}=\text{O})(\text{CO})(\text{PPh}_3)_2]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ). *p*-Tolyl isocyanate reacts with the complexes  $[\text{MHX}(\text{CO})(\text{PPh}_3)_3]$  in boiling toluene over a period of ca. 6 h ( $\text{M} = \text{Ru}$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) or in boiling ethylbenzene over a period of ca. 10 h ( $\text{M} = \text{Os}$ ,  $\text{X} = \text{Br}$ ) to yield formamido complexes  $[\text{MX}(\text{RN}=\text{CH}=\text{O})(\text{CO})(\text{PPh}_3)_2]$  analogous to the thioformamido derivatives previously obtained from aryl isothiocyanates ( $\text{ArNCS}$ ) by a similar route.<sup>3</sup> The new complexes are yellow, air-stable crystalline solids and display strong infrared bands at ca. 1540 and 1280  $\text{cm}^{-1}$  attributable to the formamide ( $\text{RN}=\text{CH}=\text{O}$ ) ligand. The ruthenium complexes display a singlet in their <sup>31</sup>P NMR spectra indicative of either

Table I. Melting Point and Analytical<sup>a</sup> Data

complex	mp, °C	% C <sup>a</sup>	% H	% N	% P
[RuCl(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	186-188	64.77 (65.65)	4.66 (4.65)	1.66 (1.70)	7.73 (7.52)
[RuBr(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	188-192	61.55 (62.23)	4.44 (4.45)	1.41 (1.61)	6.59 (7.14)
[OsBr(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	205-209	57.46 (56.48)	4.16 (4.00)	1.43 (1.46)	6.25 (6.47)
[RuH(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>b</sup>	198-200	67.18 (67.09)	5.09 (4.91)	1.32 (1.72)	8.11 (7.65)
[OsH(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	187-190	60.35 (61.56)	4.52 (4.47)	1.62 (1.59)	7.76 (7.05)
[Ru{RN-C(O)-NR}(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	194-197	68.93 (69.20)	4.89 (4.82)	2.97 (3.04)	6.52 (6.73)
[Os{RN-C(O)-NR}(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	216-220	62.74 (63.08)	4.46 (4.39)	2.25 (2.78)	
[RuH(RN=CH=NR)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>c</sup>	184-189	69.61 (69.93)	4.97 (5.56)	2.74 (3.08)	
[OsH(RN=CH=NR)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	147-150	63.84 (64.58)	4.91 (4.80)	2.25 (2.90)	6.39 (6.41)

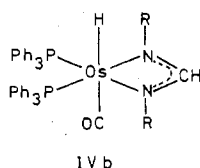
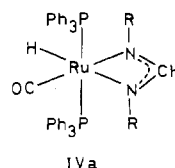
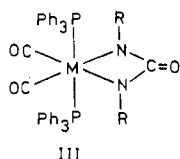
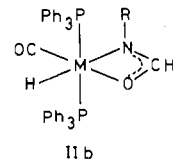
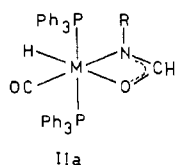
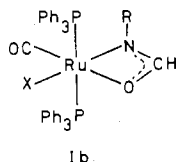
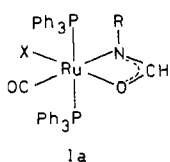
<sup>a</sup> Calculated figures given in parentheses. <sup>b</sup> Figures calculated for 4/1 dichloromethane solvate. <sup>c</sup> Figures calculated for 1/1 methanol solvate.

Table II. Spectroscopic Data

complex	ligand vib, cm <sup>-1</sup>	$\nu(\text{CO})$ , cm <sup>-1</sup>	$\nu(\text{MH})$ , cm <sup>-1</sup>	$\tau_{\text{MH}}$	$^2J(\text{PH})$ , Hz	$\tau_{\text{Me}}$	$\delta_{\text{P}}$
[RuCl(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1540, 1280	1930				7.82	33.4
[RuBr(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1540, 1280	1950				7.80	33.7
[OsBr(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1540, 1270	1910				<i>a</i>	<i>a</i>
[RuH(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1565, 1250	1910	2010	26.5 t <sup>c</sup>	20.5	7.80	43.6
[OsH(RN=CH=O)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1540, 1270	1900	2040	23.2 t	18.75	7.76	
[Ru{RN-C(O)-NR}(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	1610, 1500, 1320	2015, 1950				7.80	27.05
[Os{RN-C(O)-NR}(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	1610, 1502, 1320	2000, 1930				7.80	-0.44
[RuH(RN=CH=NR)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1540, 1505, 1280, 1270, 815	1930	<i>b</i>	23.37 t	20.0	7.74/7.90	
[OsH(RN=CH=NR)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1540, 1508, 1280, 1265, 820	1905	1940	20.54 t	12.8	7.83	

<sup>a</sup> See text. <sup>b</sup> Masked by  $\nu(\text{CO})$ . <sup>c</sup> t = triplet.

stereochemistry Ia or Ib. Since the related acetato<sup>9</sup> or trifluoroacetato<sup>10</sup> and triazenido<sup>11</sup> or formamidinato<sup>5</sup> complexes containing carbonyl ligands trans to oxygen and nitrogen donors, respectively, all show similar  $\nu(\text{CO})$  frequencies, it is not possible to distinguish between the alternative structures Ia and Ib on the basis of infrared spectroscopic evidence. The osmium complex [OsBr(RN=CH=O)(CO)(PPh<sub>3</sub>)<sub>2</sub>] gives satisfactory analytical data. However its <sup>31</sup>P and <sup>1</sup>H NMR spectra indicate that it is a complex mixture containing many if not all of the seven possible stereoisomers.



[MH(RN=CH=O)(CO)(PPh<sub>3</sub>)<sub>2</sub>]. Under relatively mild conditions (M = Ru, benzene, 15-min reflux; M = Os, toluene, 8-h reflux) the complexes [MH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>] react with

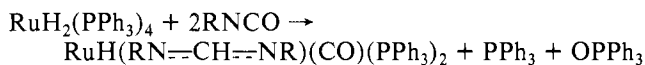
*p*-tolyl isocyanate to afford the formamido derivatives [MH(RN=CH=O)(CO)(PPh<sub>3</sub>)<sub>2</sub>] as white, air-stable microcrystalline solids. Each complex displays a singlet in its <sup>31</sup>P NMR spectrum indicative of stereochemistry IIa or IIb. However, comparison of the high-field proton NMR chemical shifts ( $\tau_{\text{MH}}$ ) recorded for the formamido complexes with those previously reported for the corresponding ruthenium and osmium acetato,<sup>9</sup> trifluoroacetato,<sup>10</sup> triazenido,<sup>11</sup> and formamidinato<sup>5</sup> derivatives strongly suggests that the ruthenium complex [RuH(RN=CH=O)(CO)(PPh<sub>3</sub>)<sub>2</sub>] and its osmium analogue contain hydride ligands trans to oxygen and nitrogen donor atoms, respectively. We therefore tentatively assign stereochemistry IIa to the ruthenium complex and stereochemistry IIb to its osmium counterpart.

Although insertion of organic isocyanates into transition metal-nitrogen<sup>12</sup> or -carbon<sup>13</sup> bonds has previously been reported, the reactions discussed above are, to the best of our knowledge, the first examples of isocyanate insertion into metal-hydrogen bonds.

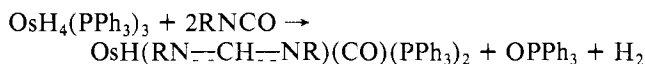
[M{RN-C(O)-NR}(CO)<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>]. Under more vigorous and/or prolonged reaction conditions (M = Ru, toluene, 5-h reflux; M = Os, toluene, 24-h reflux) cleavage of a molecule of isocyanate leading to formation of the ureylene complexes [M{RN-C(O)-NR}(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] occurs. The presence of the ureylene ligand in these products is confirmed by infrared spectroscopy [ $\nu(\text{C=O})$  ca. 1610 cm<sup>-1</sup>], and the overall stereochemistry III is established by the infrared and NMR spectroscopic data [M = Ru,  $\nu(\text{CO})$  ca. 2020 and 1950 cm<sup>-1</sup>,  $\tau_{\text{Me}}$  7.8 (s),  $\delta_{\text{PPh}_3}$  27.05 (s); M = Os,  $\nu(\text{CO})$  ca. 2000 and 1930 cm<sup>-1</sup>,  $\tau_{\text{Me}}$  7.8 (s),  $\delta_{\text{PPh}_3}$  -0.44 (s)]. An analogous ruthenium complex [Ru{R'N-C(O)-NR'}(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (R' = *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>) has previously been obtained by treatment of [Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] with R'N<sub>3</sub>, R'NCO, or R'NH-CO-NHR' in benzene.<sup>14</sup> Fragmentation and coordination of *p*-tolylsulfonyl isocyanate by complexes of rhodium, palladium, and platinum have also afforded ureylene derivatives of these metals.<sup>15</sup> Finally the ureylene-bridged complexes  $\mu$ -(diphenylureylene)-bis(tricarbonyliron) and  $\mu$ -(dimethylureylene)-bis(tricarbonyliron) have been obtained from the reaction of Fe<sub>3</sub>(CO)<sub>12</sub> with phenyl isocyanate<sup>16</sup> and methyl isocyanate<sup>17</sup> respectively.

[MH(RN=CH=NR)(CO)(PPh<sub>3</sub>)<sub>2</sub>]. Treatment of

[RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] or [OsH<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub>] with *p*-tolyl isocyanate affords the formamidinato complexes [MH(RN=CH=NR)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (M = Ru and Os, respectively). The ruthenium complex is identical with an authentic specimen previously prepared from di-*p*-tolylcarbodiimide<sup>4,5</sup> and is shown by X-ray diffraction methods to possess stereochemistry IVa.<sup>5</sup> In contrast, the less labile osmium system retains the intermediate stereochemistry IVb rather than isomerizing to the thermodynamically preferred structure IVa. Spectroscopic data (Table II) are in accord with these stereochemical assignments. Formation of the formamidinate ligand clearly involves fragmentation of at least two isocyanate moieties. The stoichiometry of the overall reaction appears to be



or



At the request of a referee we append a note on the NMR spectra of the formamide and formamidinate ligands. As we have previously noted, chelate ligands of the form X=CH=Y (X, Y = RN or S) usually show a proton resonance,  $\tau_{\text{CH}}$  ca. -5 to +2, attributable to the ligand CH group. However, in several instances the position of this resonance is such that masking by the aromatic resonances of the PPh<sub>3</sub> ligand ( $\tau_{\text{Ph}}$  2.2-2.7) occurs. Masking has already been fully documented for one of the products mentioned in the present paper, [RuH(RN=CH=NR)(CO)(PPh<sub>3</sub>)<sub>2</sub>], and the structure of this complex has been confirmed by X-ray diffraction methods.<sup>5</sup> Therefore the apparent absence of such resonances from the <sup>1</sup>H NMR spectra of the formamido and formamidinato complexes discussed above is not inconsistent with the proposed structures.

**Registry No.** I (M = Ru, X = Cl, R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 69372-56-1; I (M = Ru, X = Br, R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 69372-57-2; I (M = Os, X

= Br, R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 71597-17-6; IIa (M = Ru, R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 69372-58-3; IIb (M = Os, R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 69427-90-3; III (M = Ru, R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 69403-53-8; III (M = Os, R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 69403-54-9; IVa (R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 60939-10-8; IVb (R = *p*-Me-C<sub>6</sub>H<sub>4</sub>), 71629-32-8; carbonylchlorohydridotris(triphenylphosphine)ruthenium, 16971-33-8; bromocarbonylhydridotris(triphenylphosphine)ruthenium, 16971-34-9; carbonyldihydridotris(triphenylphosphine)ruthenium, 25360-32-1; carbonyldihydridotris(triphenylphosphine)osmium, 12104-84-6; dihydridotetrakis(triphenylphosphine)ruthenium, 19529-00-1; tetrahydridotris(triphenylphosphine)osmium, 24228-59-9; bromocarbonylhydridotris(triphenylphosphine)osmium, 16971-32-7; *p*-tolyl isocyanate, 622-58-2.

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## Platinum(II) Complexes of the Chelating Triphosphine Bis(3-(diphenylphosphino)propyl)phenylphosphine. Phosphorus-31 NMR Studies of the Cis and Trans Influence on These Model Compounds<sup>1</sup>

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A series of planar [Pt(ttp)X]<sup>+</sup> (ttp = PhP(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>; X = Cl<sup>-</sup>, NCS<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, H<sup>-</sup>, CH<sub>3</sub><sup>-</sup>, CH<sub>2</sub>CN<sup>-</sup>, COOCH<sub>3</sub><sup>-</sup>, CH<sub>2</sub>CH=CH<sub>2</sub><sup>-</sup>, and Ph<sup>-</sup>) and [Pt(ttp)Y]<sup>2+</sup> (Y = P(OMe)<sub>3</sub> and PET<sub>3</sub>) complexes have been prepared and characterized by their elemental analyses, conductivity measurements, infrared spectra, and <sup>1</sup>H and <sup>31</sup>P NMR spectra. The  $\sigma$ -bonded carbon ligands (X = methyl, cyanomethyl, and allyl) were prepared by oxidative-addition reactions on the Pt(0) compounds Pt(ttp)PPh<sub>3</sub> and Pt(ttp)CO. The SO<sub>2</sub> complex [Pt(ttp)Cl]Cl·SO<sub>2</sub> is unusual for a SO<sub>2</sub>-metal complex, as the SO<sub>2</sub> molecule is sulfur bonded to the ionic chloride to give the SO<sub>2</sub>Cl<sup>-</sup> anion, instead of being bonded either to the metal or to one of its ligands. The magnitude of the one-bond platinum-phosphorus coupling constant obtained from phosphorus-31 NMR spectra produces the trans influence series Ph<sup>-</sup> ~  $\sigma$ -allyl<sup>-</sup> > COOCH<sub>3</sub><sup>-</sup> > CH<sub>3</sub><sup>-</sup> > H<sup>-</sup> > CH<sub>2</sub>CN<sup>-</sup> > PET<sub>3</sub> > P(OMe)<sub>3</sub> > NO<sub>2</sub><sup>-</sup> > -NCS<sup>-</sup> > Cl<sup>-</sup>. As the fourth ligand (X<sup>-</sup> or Y) is varied, the changes in the cis coupling constants, <sup>1</sup>J<sub>Pt-PPH<sub>2</sub>, are smaller than the changes in the trans coupling constants, <sup>1</sup>J<sub>Pt-PPH</sub>. The  $\sigma$ -donor ligands that exert a large trans influence (e.g., CH<sub>3</sub><sup>-</sup> and CH<sub>2</sub>CH=CH<sub>2</sub><sup>-</sup>) display a small cis influence, whereas those ligands that exert a small trans influence (e.g., Cl<sup>-</sup>) produce a relatively large cis influence. The following cis influence series is deduced from the <sup>1</sup>J<sub>Pt-PPH<sub>2</sub> values: P(OMe)<sub>3</sub> > NCS<sup>-</sup> > Cl<sup>-</sup> > PET<sub>3</sub> > NO<sub>2</sub><sup>-</sup> > CH<sub>2</sub>CN<sup>-</sup> > COOCH<sub>3</sub><sup>-</sup> > H<sup>-</sup> > CH<sub>3</sub><sup>-</sup> > Ph<sup>-</sup> >  $\sigma$ -allyl<sup>-</sup>. The <sup>31</sup>P NMR spectra of several [Pt(ttp)X]<sup>+</sup> complexes (X = anionic ligand) demonstrate that the <sup>195</sup>Pt satellite patterns are not necessarily the same as the central resonance.</sub></sub>

## Introduction

A trans or cis influence is defined as the extent to which a ligand L weakens the bond trans or cis to itself, M-A, in

the ground state of a metal complex.<sup>2</sup> Recent theoretical treatments explain satisfactorily the high trans influence of ligands such as hydride and  $\sigma$ -alkyl which have strong  $\sigma$ -donor