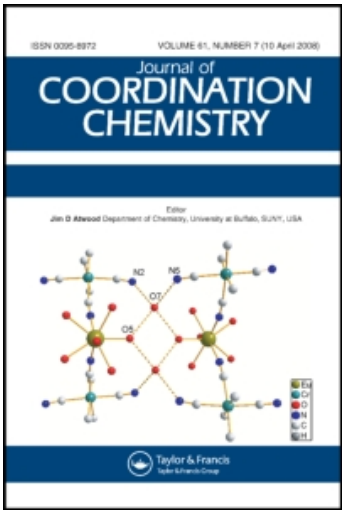

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STERIC EFFECTS ON BINDING O_2, SO_2 AND CH_3I TO SQUARE-PLANAR IRIDIUM(I) COMPLEXES, *trans*-Ir(CO)(Cl)(P(*i*-Pr)$_3$)$_2$ AND *trans*-Ir(CO)(Cl)(P(*t*-Bu)$_2$Me)$_2$

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Steric and electronic effects of phosphine ligands on binding of molecules to iridium(I) have been probed by studying reactions of O_2, SO_2 and CH_3I with *trans*-Ir(CO)(Cl)(P(*i*-Pr)$_3$)$_2$ and *trans*-Ir(CO)(Cl)(P(*t*-Bu)$_2$Me)$_2$ for comparison to known reactions with *trans*-Ir(CO)(Cl)L$_2$ (L = PPh_3, P(p-tolyl)$_3$ and PCy_3). Reaction of O_2 is significantly retarded by increasing size of the ligand while reaction of SO_2 is essentially unaffected by the nature of the phosphine ligand. Reaction of CH_3I with *trans*-Ir(CO)(Cl)(P(*t*-Bu)$_2$Me)$_2$ produces two products which have been characterized by NMR and infrared spectroscopy.

Keywords: Oxidative addition; dioxygen; sulfur dioxide; iridium(I); steric effects

Addition reactions of small molecules to square-planar iridium(I) complexes have been extensively studied, since Vaska's initial investigations began in 1961 with O_2 addition to Ir(CO)Cl(PPh$_3$)$_2$.[1] Complexes of the general type Ir(CO)X(PR$_3$)$_2$ allow changes in reactivity of the metal center by varying the phosphines to change the electron density at the metal or the steric crowding around the metal. Variations in X allow further changes in electron density. Subsequent reactions of these complexes give an indication of the effect that steric and electronic properties have on reactivity towards molecules such as CH_3I and O_2.

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This study is concerned with two alkyl phosphines, tri-*iso*propyl phosphine ($P(i\text{-}Pr)_3$) and di-*tert*butyl methyl phosphine ($P(t\text{-}Bu)_2Me$). Both sterically and electronically they are similar: Tolman's cone angle[2] is 160° for $P(i\text{-}Pr)_3$ and 161° for $P(t\text{-}Bu)_2Me$ and χ from Tolman's[3] measurements is $3.0\,cm^{-1}$ for $P(i\text{-}Pr)_3$ and $2.6\,cm^{-1}$ for $P(t\text{-}Bu)_2Me$. This manuscript examines the reactions of *trans*-$Ir(CO)Cl(P(i\text{-}Pr)_3)_2$ and *trans*-$Ir(CO)Cl(P(t\text{-}Bu)_2Me)_2$) with O_2, SO_2 and CH_3I. Interest in reactions of such molecules arises due to their importance in catalytic cycles; for instance oxidative addition of CH_3I is an important step in the Monsanto acetic acid process.[4] Thus investigation of this type of reaction aids understanding of the various steps occurring during catalysis. Reactions of SO_2 are of further interest due to environmental concerns.

EXPERIMENTAL

Materials

$IrCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey. $P(i\text{-}Pr)_3$ was purchased from Strem Chemical Company. Methyl lithium (MeLi), iodomethane (CH_3I) and di-*tert*butylchlorophosphine ($P(t\text{-}Bu)_2Cl$) were purchased from Aldrich. $P(t\text{-}Bu)_2Me$ was prepared from $P(t\text{-}Bu)_2Cl$ and MeLi by a previously published method.[5] Anhydrous SO_2 was purchased from Matheson. All of these were used without further purification. Solvents used outside the glove box were used as received without further purification. THF was purified by refluxing over CaH_2, distilling into Na/benzophenone, refluxing over Na/benzophenone and distilling into an air-free container. Deuterated solvents were dried by stirring overnight using finely divided CaH_2, followed by vacuum distillation into an oven-dried pressure tube fitted with a Teflon stopcock.

Instrumentation

Infrared spectra were recorded on a Mattson Polaris Fourier Transform spectrophotometer in the range $2200\text{–}400\,cm^{-1}$. NMR spectra, both ^1H and ^{31}P, were recorded on a Varian VXR-400 spectrophotometer. For ^1H NMR residual solvent peaks were used as an internal reference. An external H_3PO_4 reference which was assigned a shift of 0.00 ppm was used for ^{31}P NMR; ^{31}P spectra were proton decoupled.

Preparation

All syntheses were carried out under an atmosphere of argon or nitrogen, using an argon-filled glove box, Schlenk or high vacuum techniques.

trans-Ir(CO)(Cl)(P(i-Pr)$_3$)$_2$ was prepared by a previously published method.[6] Yield: 1.4 g, 89% IR (CH_2Cl_2): ν_{CO} 1935 cm^{-1} (Literature value:[7] IR (CH_2Cl_2): 1935 cm^{-1}) ^1H NMR (CD_2Cl_2): 2.65 (m) (2H, J = 4.0 Hz) and 1.3 (q) (12H, J = 6.9 Hz) ppm; ^{31}P NMR (CD_2Cl_2): 42.1 ppm.

trans-Ir(CO)(Cl)(P(t-Bu)$_2$Me)$_2$ was prepared using the same method as for the P(*i*-Pr)$_3$ derivative.[6] (Yield: 0.4 g, 31%) IR (CH_2Cl_2): ν_{CO} 1932 cm^{-1} (Literature values:[8] IR (Nujol): ν_{CO} 1926 cm^{-1} (Benzene): ν_{CO} 1937 cm^{-1}) ^1H NMR (C_7D_8): 1.4 (t) (18H) and 1.6 (br) (3H) ppm (Literature values:[8] ^1H NMR: 1.3 (t) (*t*-Bu), 1.5 (t) (CH_3) ppm) ^{31}P NMR (C_7D_8): 38.2 ppm.

Reactions

Reactions of *trans*-Ir(CO)(Cl)(P(*i*-Pr)$_3$)$_2$ and *trans*-Ir(CO)(Cl)(P(*t*-Bu)$_2$Me)$_2$ with various molecules were performed on a preparative and on NMR scale. NMR scale reactions were prepared in an inert atmosphere glove box (~20 mg iridium complex in CD_2Cl_2) in an NMR tube equipped with a vacuum adapter. The tube was removed from the glove box and placed on a high vacuum line where the reactant molecule was added and the tube sealed. Spectra were recorded periodically. Reactions with O_2 and SO_2 were carried out using a pressure of 600 mmHg. The O_2/SO_2 mixture consisted of 300 mmHg pressure of each gas. The MeI reaction used a ten fold excess of the reactant.

Preparative-scale reactions were conducted in Schlenk flasks with the iridium complex (100 mg) added in the inert atmosphere glove box. The flask was sealed and transferred to a hood where the solid was dissolved in CH_2Cl_2 and the reactant molecule added. The O_2 and SO_2 reactions were carried out by allowing the gas to pass over the solution for 15 min. For reactions involving mixtures of gases, they were added on the high vacuum line using a Schlenk flask equipped with an adaptor (300 mmHg of each gas). MeI was added in ten-fold excess. Excess iodide was added in the form of $CH_3PPh_3^+I^-$. Infrared spectra were recorded periodically.

Results of the experiments are given in Tables I and II.

RESULTS

Neither of the complexes reacted completely with O_2; both form an equilibrium mixture of O_2 adduct and starting material, the slightly smaller P(*i*-Pr)$_3$ ligand reacts to a greater extent than P(*t*-Bu)$_2$Me, forming ~75% O_2 adduct against ~60% for the P(*t*-Bu)$_2$Me complex. The change in ν_{CO} (Table I) is comparable to that found for the PPh_3 analogue

TABLE I Spectroscopic characterization of the products

Compound	*IR(CH_2Cl_2) (cm^{-1})*	*^{31}P NMR(CD_2Cl_2)*
trans-Ir(CO)(Cl)(P(*i*-Pr)$_3$)$_2$	1935	42.1
Ir(CO)(Cl)(O_2)(P(*i*-Pr)$_3$)$_2$	1994	10.5
Ir(CO)(Cl)(SO_2)(P(*i*-Pr)$_3$)$_2$	1999	41.4
Ir(CO)(Cl)(CH_3)(I)(P(*i*-Pr)$_3$)$_2$	2013	−9.7[a]
Ir(CO)(Cl)(SO_4)(P(*i*-Pr)$_3$)$_2$	2051	18.4
trans-Ir(CO)(Cl)(P(*t*-Bu)$_2$Me)$_2$	1932	38.2
Ir(CO)(Cl)(O_2)(P(*t*-Bu)$_2$Me)$_2$	2002	5.7
Ir(CO)(Cl)(SO_2)(P(*t*-Bu)$_2$Me)$_2$	1997	24.8
Ir(CO)(Cl)(CH_3)(I)(P(*t*-Bu)$_2$Me)$_2$	2013 and 2030	47 and 8.0[b,c]
Ir(CO)(Cl)(SO_4)(P(*t*-Bu)$_2$Me)$_2$	2051	8.6

[a]The Ir–CH_3 is at 0.9(t) ppm (J_{P-H} = 6.8 Hz). [b]The Ir–CH_3 is at 0.9(t) ppm (J_{P-H} = 6.4 Hz). [c]With excess I^-, added as CH_3PPh_3I, only the 2030 cm^{-1} and 47 ppm product was seen.

TABLE II Products of the reactions of *trans*-Ir(CO)(Cl)L_2

L	*Reactant molecule*	*Product*
P(*i*-Pr)$_3$	O_2	Ir(CO)(Cl)(O_2)L_2 (75% with starting complex)
PMe(*t*-Bu)$_2$	O_2	Ir(CO)(Cl)(O_2)L_2 (60% with starting complex)
P(*i*-Pr)$_3$ or PMe(*t*-Bu)$_2$	SO_2	Ir(CO)(Cl)(SO_2)L_2
P(*i*-Pr)$_3$ or PMe(*t*-Bu)$_2$	SO_2 (103 ppm in air)	Ir(CO)(Cl)(SO_2)L_2 with starting complex
P(*i*-Pr)$_3$ or PMe(*t*-Bu)$_2$	SO_2/O_2	Ir(CO)(Cl)(SO_4)L_2
P(*i*-Pr)$_3$	CH_3I	Ir(CO)(Cl)(CH_3)(I)L_2
PMe(*t*-Bu)$_2$	CH_3I	two products – see Discussion

(1967–2015 cm^{-1}).[9] For both P(*i*-Pr)$_3$ and P(*t*-Bu)$_2$Me the oxygen could be removed by refluxing in toluene, recovering the starting material. The NMR scale reaction showed the effect of a higher [O_2] with P(*i*-Pr)$_3$ reacting completely in one day and P(*t*-Bu)$_2$Me reacting to give ~85% O_2 adduct.

Reaction with SO_2 is similar in both cases, rapid at room temperature to give a single product. The P(*i*-Pr)$_3$ complex reacts faster, taking 30 min to completely react, while the P(*t*-Bu)$_2$Me complex took 45 min. The products are characterized by the ν_{CO} and ^{31}P, which correspond with the data for PPh_3 complexes (ν_{CO} shifts from 1967 to 2021 cm^{-1}).[9] The starting material could be recovered by refluxing in toluene overnight.

In reactions with mixtures of SO_2 and O_2 there is a kinetic preference for SO_2 binding, but a thermodynamic preference for O_2 binding. Thus the SO_2 adduct forms initially, before conversion to the sulfate complex or the O_2 complex depending on the concentrations.

The reaction with a 50/50 mixture of O_2 and SO_2 led to formation, shown by IR, of the sulfate in both cases; ν_{CO} for the SO_4 adduct[10] of the PPh_3 complex is 2045 cm^{-1}. The intermediate could not be clearly identified using IR since for both phosphines the ν_{CO} values of the O_2 and SO_2 adducts

are very close. In the ^{31}P NMR both the O_2 and SO_2 products are clearly differentiated. The initial reaction forms only the SO_2 adduct, which is then followed by formation of the O_2 adduct. After one day there is just SO_2 adduct and O_2 adduct. Over the course of time several other unidentified peaks appear, along with gradual formation of the sulfate complex. After 10 days there is no further reaction, the peaks correspond to the SO_2 adduct, sulfate product, a small amount of O_2 adduct and the degradation product of the O_2 complex.

The addition of CH_3I to *trans*-Ir(CO)(Cl)(P(*i*-Pr)$_3$)$_2$ proceeded to a single product after 4 h at room temperature. Characterization data (Table I) are in agreement with previous studies:[9] ν_{CO} for the PPh_3 analogue with CH_3I is 2045 cm^{-1} and ^1H NMR has a triplet for the Ir–CH_3 (literature value[11] for Ir–CH_3 of the PPh_3 analogue 0.98 ppm (t, J = 5.7 Hz), which is similar to the data for both of the complexes (Table I). The P(*t*-Bu)$_2$Me complex gave two products, one of these corresponds to the product seen for the P(*i*-Pr)$_3$ complex. Addition of excess iodide to the reaction gave only the product with a higher ν_{CO}. The ^1H NMR of this product had a triplet for Ir–CH_3 and two doublets for the P–Me signals indicating *cis*-P(*t*-Bu)$_2$Me ligands.

DISCUSSION

Large, strongly-donating phosphine ligands such as PCy_3, P(*i*-Pr)$_3$ and P (*t*-Bu)$_2$Me are important in catalysis and organometallic chemistry. Our earlier report on reactions of *trans*-Ir(CO)(Cl)(PCy_3)$_2$ showed that reactions with H_2 and O_2 were inhibited in comparison to *trans*-Ir(CO)(Cl)(PPh_3)$_2$ while reactions with Cl_2 and SO_2 were unaffected.[12] Such reactivity changes with ligand offer the possibility to alter the selectivity of binding a molecule to a metal center by changing the ligands.

The ligands P(*i*-Pr)$_3$ and P(*t*-Bu)$_2$Me are slightly smaller than PCy_3 in cone angle, although a recent study of enthalpies of reaction indicated P(*t*-Bu)$_2$Me to be bulkier than PCy_3.[13]

For reaction with O_2 where the smaller phosphines, PPh_3 and P(*p*-tolyl)$_3$, react completely with O_2 at room temperature, but the much larger PCy_3 does not react at all, the two phosphines (P(*i*-Pr)$_3$ and P(*t*-Bu)$_2$Me) show some reactivity with O_2. Both *trans*-Ir(CO)(Cl)(P(*i*-Pr)$_3$)$_2$ and *trans*-Ir(CO)(Cl)(P(*t*-Bu)$_2$Me)$_2$ show comparable reactivity toward O_2, substantially more reactivity than *trans*-Ir(CO)(Cl)(PCy_3)$_2$. Indeed the reaction of O_2 with *trans*-Ir(CO)(Cl)L_2 is very sensitive to the size of L. The fact that

SO_2 reacts faster than O_2 has been attributed to electronic effects.[12] In contrast to O_2, which is very sensitive to the ligand L in *trans*-Ir(CO)(Cl)L_2, SO_2 reacts without any major effect by L. The previous reactions of SO_2 for $L = PCy_3$[12] are also observed here for $L = P(i\text{-}Pr)_3$ and $P(t\text{-}Bu)_2Me$. Reactions occur in a few minutes.

The facile reaction of SO_2 in comparison to O_2 with *trans*-Ir(CO)(Cl)L_2 (L = a bulky phosphine ligand) is also observed for mixtures of O_2 and SO_2. The SO_2 adduct is formed rapidly, though ultimately the O_2 adduct and the sulfate complex are formed. For $L = P(i\text{-}Pr)_3$ and $P(t\text{-}Bu)_2Me$ the behavior with mixtures of O_2 and SO_2 is more similar to $L = P(p\text{-tolyl})_3$ than to PCy_3 where neither O_2 coordination nor sulfate formation is observed.

Reaction of MeI with *trans*-Ir(CO)(Cl)$(P(i\text{-}Pr)_3)_2$ occurs giving a six-coordinate product with *trans* methyl and iodide groups similar to reactions of the $P(p\text{-tolyl})_3$ or PPh_3 analogues. The $P(t\text{-}Bu)_2Me$ complex reacts with MeI to give two products. One product ($\nu_{CO} = 2013\,cm^{-1}$ and $^{31}P = 8.0$ ppm) is the direct analogue of the product observed for the $P(i\text{-}Pr)_3$ complex. The other product, prepared exclusively in an excess of I^-, has a $\nu_{CO} = 2030\,cm^{-1}$, ^{31}P of 47 ppm, a triplet for the Ir–CH_3 and doublets for the P–Me groups. The doublets indicate *cis*-$P(t\text{-}Bu)_2Me$ groups and an absence of virtual coupling. However, the reason for such large groups to be *cis* is not obvious.

One example found in the literature, that does not involve η^2 addition, is with allyl chloride and Ir(CO)Cl$(PPhMe_2)_2$,[14] the initial product contains *cis* phosphines, shown by NMR doublets, which then isomerizes to the *trans* product *via* Cl^- dissociation. The difference here is that $P(t\text{-}Bu)_2Me$ is a bulky ligand and all previous work indicates that bulky phosphines prefer to be *trans*. Ligand dissociation to give the monophosphine can be ruled out since there was no signal for free phosphine in the ^{31}P spectrum. In addition to the ^1H NMR data, the IR data also correlate to a study[15] of $IrCl_3(CO)(PMe_2Ph)_2$ isomers. With the two phosphines *cis* and CO *trans* to Cl the ν_{CO} is $9\,cm^{-1}$ higher and with CO *trans* to the phosphine $28\,cm^{-1}$ higher, than the same complex with *trans* phosphines; so octahedral complex with *cis* phosphines would be expected to have a higher ν_{CO} than the corresponding structure with *trans* phosphines, as observed.

CONCLUSION

This study has furthered our understanding of ligand steric and electronic effects. In every case except one the reactivity would be as expected given

the size and electronic effects of the ligands. The one exception is the reaction of the $P(t\text{-}Bu)_2Me$ complex with CH_3I, which appears to form one product containing *cis* phosphines. This would not be favored on steric grounds, but it may be that the combination of the large *t*-butyl groups and smaller methyl group, allow the *cis* form to be more stable.

References

[1] L. Vaska and J.W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).
[2] C.A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
[3] C.A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
[4] D. Forster and T.W. DeKleva, *J. Chem. Ed.*, **63**, 204 (1986).
[5] W.D. Jones and V.L. Kuykendall, *Inorg. Chem.*, **12**, (1990).
[6] J.P. Collman and J.W. Kang, *J. Am. Chem. Soc.*, **89**, 944 (1967).
[7] F. Faraone, P. Piraino and R. Pietropaolo, *J. Chem. Soc. Dalton*, 1625 (1973).
[8] B.L. Shaw and R.E. Steinbank, *J. Chem. Soc.* (*A*), 3716 (1971).
[9] L. Vaska, *Accs. Chem. Res.*, **1**, 335 (1968).
[10] J. Valentine, D. Valentine and J.P. Collman, *Inorg. Chem.*, **10**, 219, (1971).
[11] M. Crespo and R.J. Puddephatt, *Organometallics*, **12**, 2548 (1987).
[12] C.A. Miller, C.H. Lake, M.R. Churchill and J.D. Atwood, *Organometallics*, **14**, 5442 (1995).
[13] C. Li, M. Ogasawara, S.P. Nolan, and K.G. Caulton, *Organometallics*, **15**, 4900 (1996).
[14] B.L. Shaw and A.J. Deeming, *J. Chem. Soc.* (*A*), 1562 (1969).
[15] B.L. Shaw and A.C. Smithies, *J. Chem. Soc.* (*A*), 2784 (1968).