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PREPARATION AND CHARACTERIZATION OF FIVE AND SIX-COORDINATED IRIDIUM(III) COMPLEXES CONTAINING *S*-, *O*- OR *O,O'*-TRIFLUOROMETHANESULFINATO GROUPS

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Summary

The oxidative addition of trifluoromethanesulfonyl chloride to *trans*-{IrX-(CO)[P(C₆H₅)₃]₂} yields as the only product an iridium(III) complex, {IrXCl-(OS(O)CF₃)(CO)[P(C₆H₅)₃]₂} (Ia, X = Cl; Ib, X = Br) in which the *O*-sulfinato group is *trans* to the carbonyl ligand. This is in contrast to the behavior of hydrocarbon sulfonyl halides which have previously been found to give exclusively *S*-bonded forms with the sulfinato group *trans* to chloride. The *S*- and *O,O'*-trifluoromethanesulfinato isomers of the compound {IrCl₂(O₂SCF₃)[P(C₆H₅)₃]₂} have been prepared and characterized. Addition of carbon monoxide or pyridine to either of these isomers gives {IrCl₂(-S(O)₂CF₃)[P(C₆H₅)₃]₂ · B} (B = CO or C₅H₅N) in which the added Lewis base is *trans* to an *S*-sulfinato group.

Introduction

The sulfinato ligand is of interest in organometallic chemistry because of its formation in sulfur dioxide insertion reactions of metal carbon bonds and its involvement in the desulfonation of sulfonyl halides catalyzed by metal complexes [1,2,3]. Sulfur-bonded sulfinates are the most numerous in transition metal organometallic compounds [1,2]. Insertion of sulfur dioxide into metal-carbon bonds leads to *S*-sulfinates as the isolable product, although *O*-sulfinates may be the kinetically controlled product [1,4]. Oxidative addition of a wide range of alkyl- and arylsulfonyl halides to low valent complexes of the platinum metals has given exclusively *S*-sulfinato complexes [5-9]. The *O*-sulfinato complex *trans*-{Ir[OS(O)C₆H₄CH₃]CO(PPh₃)₂} has been prepared from Vaska's complex by a metathetical reaction. Oxidation of this complex by dioxygen yields a product which contains the *S*-sulfinato group [10]. We wish to report the synthesis and properties of five and six-coordinated complexes of iridium(III) which contain an *S,O*- or bidentate trifluoromethanesulfinato ion. In the light of our

TABLE 1
INFRARED DATA (cm^{-1} , Nujol) ^{a, b}

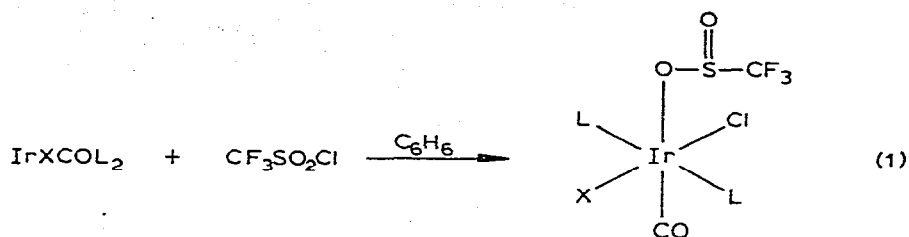
Complex ^c	$\nu(\text{C}\equiv\text{O})$	$\nu_{\text{as}}(\text{S}-\text{O}-\text{Ir})$	$\nu(\text{S}=\text{O})$	$\nu_{\text{as}}(-\text{S}(\text{O})_2-)$	$\nu_{\text{sym}}(-\text{S}(\text{O})_2-)$	$\nu(\text{Ir}-\text{Cl})$	Bond type
$\text{IrCl}_2(-\text{OS}(\text{O})\text{CF}_3)(\text{CO})\text{L}_2$	2080	888	1120			338	O
$\text{IrClIr}(-\text{OS}(\text{O})\text{CF}_3)(\text{CO})\text{L}_2 \cdot \text{C}_6\text{H}_6$	2080	892	1118			334	O
$\text{IrCl}_2(-\text{S}(\text{O})_2\text{CF}_3)\text{L}_2$				1280	1075	330	S
$\text{IrCl}_2(\text{O}, \text{O}'-\text{SCF}_3)\text{L}_2$		935	1040			329	O, O'
$\text{IrCl}_2(-\text{S}(\text{O})_2\text{CF}_3)(\text{CO})\text{L}_2$	2100			1262	1076	338	S
$\text{IrCl}_2(-\text{S}(\text{O})_2\text{CF}_3)(\text{C}_5\text{H}_5\text{N})\text{L}_2$				1250	1070	331	S

^a Bands due to $\text{P}(\text{C}_6\text{H}_5)_3$ groups are not included. ^b Bands due to the CF_3 group appear as broad peaks between 1140 and 1200 cm^{-1} . ^c L = $\text{P}(\text{C}_6\text{H}_5)_3$.

findings, previous observations [7] on the rate of migration of perfluoro groups in five coordinated sulfinato complexes have been reinterpreted.

Results and discussion

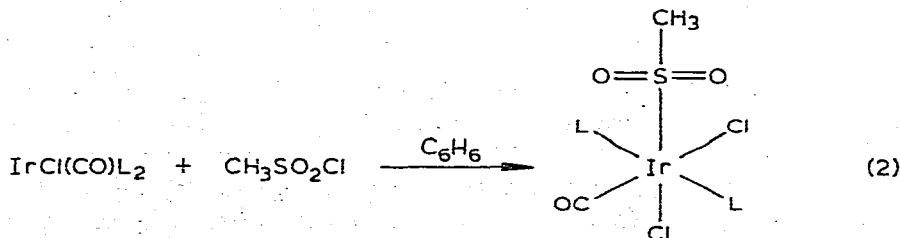
Addition of trifluoromethanesulfonyl chloride, $\text{CF}_3\text{SO}_2\text{Cl}$, to Vaska's complex or its bromo analog, yields the complexes Ia or Ib in which an *O*-sulfinato group is incorporated *trans* to the carbonyl ligand (eq. 1).



Ia: X = Cl, L = PPh_3

Ib: X = Br, L = PPh_3

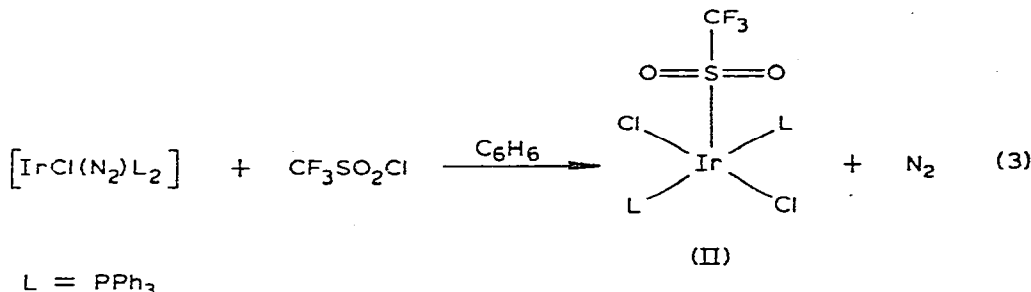
This structure is supported by the following evidence. Compound Ia has a single IR band (Table 1) at 329 cm^{-1} characteristic of $\nu(\text{Ir}-\text{Cl})$ for chloride *trans* to chloride [11,12]. In the S—O region of the IR two bands are assigned as $\nu(\text{S}=\text{O})$, 1120 cm^{-1} , and $\nu(\text{Ir}-\text{O}-\text{S})$, 888 cm^{-1} . These are characteristic of an *O*-sulfinato group [2]. Similar bands are found in the IR spectrum of the bromo analog. Mutually *trans* phosphine ligands are indicated by the relative intensity of the pair of weak bands at 1675w and $1690\text{vw} \text{ cm}^{-1}$ [7]. The correlation of these band intensities with the relative positions of the phosphine ligands has not been well established; however, oxidative addition products of Vaska's complex in which the triphenylphosphine ligands are *cis* are very rarely encountered [13]. The products of reaction 1 contrast in two respects with those of the oxidative addition of hydrocarbon sulfonyl chlorides to a wide range of iridium(I) complexes [5,7,8,9]: (1) alkyl- and arylsulfonyl halides have been found to give only *S*-sulfinates and (2) the addition products obtained in prior work incorporate the sulfinato group *trans* to chloride, not carbon monoxide. We have rechecked the results of Collman and Roper [5], who reported no $\nu(\text{Ir}-\text{Cl})$ data, and confirmed that the isomer obtained by the addition of methanesulfonyl chloride to Vaska's complex is that shown in eq. 2.



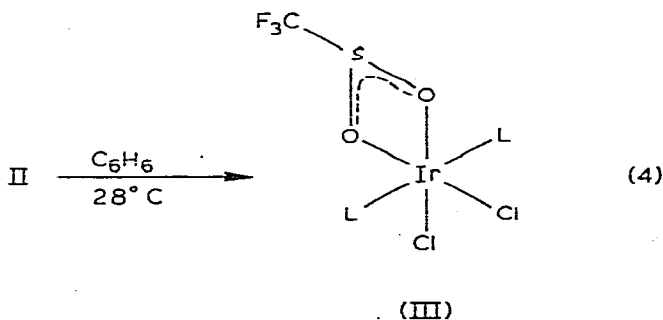
L = PPh_3

The values of $\nu_{as}(\text{SO}_2)$, 1220 cm^{-1} , $\nu_{sym}(\text{SO}_2)$, 1070 cm^{-1} and $\nu(\text{CO})$ at 2090 cm^{-1} correspond to those reported in the original work. Two weak bands at 312 and 272 cm^{-1} in the $\nu(\text{Ir}-\text{Cl})$ region are consistent with a chloride *trans* to carbon monoxide and one *trans* to an *S*-sulfinato group, respectively [11]. The same geometric and linkage isomer also has been obtained when the ligand L is dimethylphenylphosphine [9] or methylphenylphosphine [8].

A coordinatively unsaturated sulfinato complex can be obtained by the following method. Addition of trifluoromethanesulfonyl chloride to *trans*- $[\text{IrCl}(\text{N}_2)\text{L}_2]$ yields a brown product, II, (reaction 3).

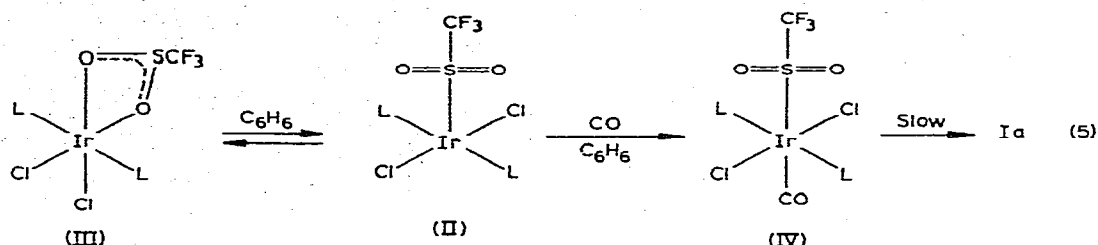


This compound is characterized by $\nu(\text{Ir}-\text{Cl})$ at 330 cm^{-1} , $\nu_{as}(\text{SO}_2-)$ at 1280 cm^{-1} and $\nu_{sym}(\text{SO}_2-)$ at 1075 cm^{-1} . These bands are consistent with *trans* chloro-ligands and an *S*-sulfinato ion [2,11]. The complex is monomeric in chloroform but is not sufficiently soluble to obtain a ^{19}F NMR spectrum. Hydrocarbon analogs of II have been obtained by Kubota and Leoffler [7]. The known examples of five coordinated iridium(III) complexes are believed to have a square pyramidal geometry [7,12]. Upon stirring a suspension of complex II in benzene it isomerizes to a yellow form, III, which is also monomeric in chloroform (eq. 4).



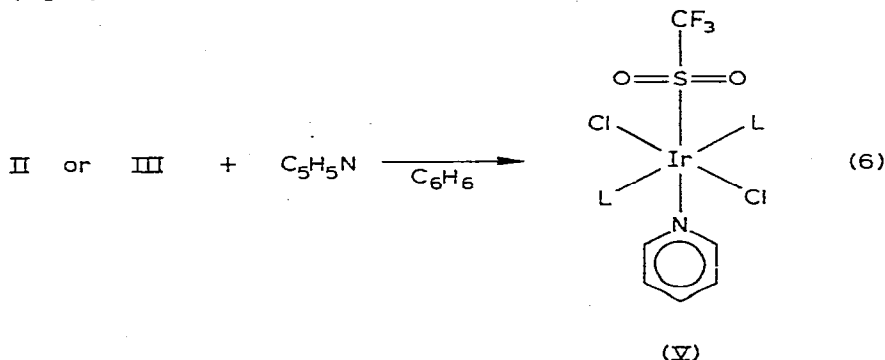
This complex, III, is characterized by a single band in the $\nu(\text{Ir}-\text{Cl})$ region at 329 cm^{-1} , which is appropriate for Cl *trans* to oxygen [11], and there is a shift in the S—O vibrational modes to 1040 and 935 cm^{-1} . These bands are consistent with a structure in which the sulfinato group acts as a chelating ligand [2].

Complexes II and III are probably in rapid equilibrium in solution. Addition of carbon monoxide to either complex dissolved in benzene gives the carbonyl adduct having an *S*-sulfinato group, IV, (eq. 5).



Spectral data for compound IV are consistent with the given structure. There is a single $\nu(\text{Ir}-\text{Cl})$ band at 338 cm^{-1} (Cl *trans* to Cl) [11] and the S—O bands, $\nu_{\text{as}}(\text{SO})_2$ 1262 cm^{-1} and $\nu_{\text{sym}}(\text{SO}_2)$ 1076 cm^{-1} , are characteristic of the S-bonded form [11]. $\nu(\text{CO})$ is at 2100 cm^{-1} , characteristic of CO *trans* to a good π -acceptor ligand [2]. The S-sulfinato complex, IV, is the kinetically controlled product. It will slowly isomerize to the O-sulfinato complex, Ia, in benzene or methylene chloride solution. Conversion is complete in about 5 h at room temperature. The slow rate at which compound IV isomerizes to the O-sulfinato isomer, Ia, makes it unlikely that an S-sulfinate is the initial oxidative addition product in reaction 1. We have found no evidence for linkage isomerization in the methylsulfinato analog of IV which was prepared by Kubota and Loeffler [7]. However, the methyl derivative loses SO_2 at a rate which would make its loss competitive with the rearrangement.

Pyridine also reacts with either II or III to produce an S-sulfinato complex (eq. 6).



The IR spectrum of compound V clearly shows that the sulfinato group is S-bonded $\nu_{\text{sym}}(\text{SO}_2-)$ 1085 and $\nu_{\text{as}}(\text{SO}_2-)$ 1275 cm^{-1} . The single band at 332 cm^{-1} is indicative of mutually *trans* chloro ligands.

The results of reactions 5 and 6 indicate that interconversion of the S-bonded and bidentate forms of the complex is facile. It does not appear that a monodentate, O-sulfinate is present to a significant extent. If it were, the thermodynamically most stable carbonyl adduct, Ia, would likely be an observed product of carbon monoxide addition in reaction 5.

Coordinatively unsaturated hydrocarbon sulfonyl complexes have been found to readily undergo a migration reaction in solution, yielding alkyl or aryl complexes and sulfur dioxide. Heating of the trifluoromethanesulfinato compound, II, in refluxing xylene for 48 h yields an olive green residue whose IR spectrum still shows bands due to the sulfonyl and trifluoromethyl groups in the 1100—

TABLE 2
 ANALYTICAL DATA (FOUND (CALC.)).

Complex ^a	Color	M.p. (°C)	C	H	Cl	Molecular weight
$\text{IrCl}_2(-\text{OS}(\text{O})\text{CF}_3)(\text{CO})\text{L}_2$	Pale yellow	261	48.46 (48.11)	3.46 (3.19)	7.19 (7.47)	
$\text{IrClBr}(-\text{OS}(\text{O})\text{CF}_3)(\text{CO})\text{L}_2 \cdot \text{C}_6\text{H}_6$	Pale yellow	188	49.48 (49.33)	3.43 (3.39)		
$\text{IrCl}_2(-\text{S}(\text{O})_2\text{CF}_3)\text{L}_2$	Brown	140-5	48.31 (48.26)	3.51 (3.28)	8.33 (7.81)	930 (921)
$\text{IrCl}_2(\text{O},\text{O}'\text{-SCF}_3)\text{L}_2$	Yellow	130-2	47.89 (48.26)	3.75 (3.28)	7.15 (7.81)	923 (921)
$\text{IrCl}_2(-\text{S}(\text{O})_2\text{CF}_3)(\text{CO})\text{L}_2$	Pale yellow	260	48.33 (48.11)	3.39 (3.19)	8.26 (7.47)	
$\text{IrCl}_2(-\text{S}(\text{O})_2\text{CF}_3)(\text{C}_5\text{H}_5\text{N})\text{L}_2$	Pale yellow	123-6	50.05 (51.17)	4.01 (3.58)		

^a L = P(C₆H₅)₃.

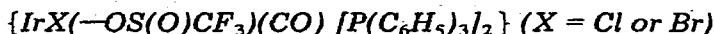
1300 cm⁻¹ region. Infrared spectra of the volatile products of the thermal decomposition of solid II in vacuo at 220°C indicate the presence of benzene, hydrogen chloride and sulfur dioxide but these were not quantified. It can be concluded that the trifluoromethyl group undergoes migration reactions in sulfonyl compounds much less readily than hydrocarbon groups. This parallels the behavior of fluorocarbon groups in acyl complexes [12,14].

Kubota and Leoffler have reported that the pentafluorophenyl group in $\text{IrCl}_2(\text{S}(\text{O})_2\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ migrates very rapidly to give the perfluoroaryl-sulfur dioxide complex $\{\text{IrCl}_2(\text{C}_6\text{F}_5)(\text{PPh}_3)_2\text{SO}_2\}$. A re-examination [15] of their data suggests that the rapid reaction they interpreted as a migration of the pentafluorophenyl group from sulfur to iridium was in fact the rearrangement of the *S*-sulfinato complex to the bidentate *O,O'*-sulfinato isomer as in reaction 4. The infrared bands they observed in the product at 1060 and 967 cm⁻¹ were assigned in the original work [7] to coordinated sulfur dioxide (in $\{\text{IrCl}_2(\text{C}_6\text{F}_5)(\text{PPh}_3)_2 \cdot \text{SO}_2\}$) but are consistent with the product actually being $\{\text{IrCl}_2(\text{O},\text{O}'\text{-SC}_6\text{F}_5)(\text{PPh}_3)_2\}$ for which the sulfur-oxygen vibrational modes occur in this region of the IR spectrum [2]. Carbonylation of the rearrangement product produces a product in which bands at 1060w and 962m cm⁻¹ remain in the IR spectrum. The presence of these bands after carbonylation would support the belief that the sulfinato group remains intact [15].

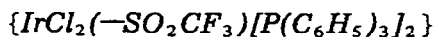
Experimental

The compounds *trans*- $\{\text{IrX}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (X = Cl or Br) [16], *trans*- $\{\text{IrCl}(\text{N}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ [17] and $\{\text{IrCl}_2(\text{S}(\text{O})_2\text{CH}_3)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ [5] were prepared by methods in the literature. Trifluoromethanesulfonyl chloride (PCR, Inc.) was stored in vacuo in a container with a teflon stopcock, as were dried benzene and toluene. Reaction mixtures including CF₃SO₂Cl were prepared in vacuo but subsequent work-up was carried out using bench-top methods. Infrared spectra were obtained on a Perkin-Elmer Model 621 spectrometer. Samples were prepared as Nujol mulls between cesium iodide plates. Molecular weights were determined

in chloroform using a Mechrolab 301A osmometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

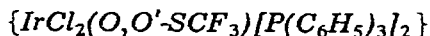


Trifluoromethanesulfonyl chloride (0.1 ml) and benzene (4 ml) were condensed onto Vaska's complex or its bromo analog (0.3 g) at 77 K in vacuo. The mixture was warmed to room temperature and stirred for 3 min. The resulting pale yellow solid was recovered, washed with benzene (1 ml) and ether and dried in vacuo. Yield 0.25 g.

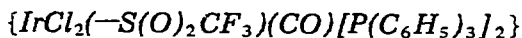


Trifluoromethanesulfonyl chloride (0.15 ml) and toluene (10 ml) were condensed onto *trans*- $\{IrCl(N_2)[P(C_6H_5)_3]_2\}$ (0.5 g) at 77 K. The mixture was warmed to 0°C and stirred for 15 min. The resulting brown solid was recovered as rapidly as possible on a filter, washed with cold toluene and dried in vacuo. Yield 0.33 g.

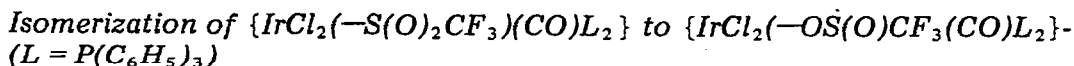
In some preparations the brown solid begins to turn yellow in the filter. Neither light nor oxygen apparently caused this change but it may be caused by washing with polar solvents. The yellow color is due to the presence of the *O, O'*-sulfinato isomer (see the following preparation).



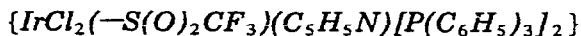
A suspension of the brown *S*-sulfinato isomer, $\{IrCl_2(-S(O)_2CF_3)(PPh_3)_2\}$, from the previous preparation (0.5 g) was stirred in benzene (10 ml) at room temperature for 20 h. Filtration gave the *O*-bonded isomer as a bright yellow solid which was washed with ether and dried in vacuo. Yield 0.3 g.



Into either the *S*- or *O, O'*-sulfinato form of $\{IrCl_2(SO_2CF_3)(PPh_3)_2\}$ (0.1 g) in benzene (2 ml) was bubbled carbon monoxide for 3–4 min. The resulting pale yellow solid was recovered and washed with ether. Yield 0.08 g.



The IR spectrum of a solution of the carbonyl-*S*-sulfinato complex in methylene chloride was recorded periodically. The band at 2100 cm^{-1} characteristic of the *S*-bonded isomer gradually decreased in intensity while that at 2080 cm^{-1} characteristic of the *O*-bonded isomer increased. The reaction was complete within 5 h at room temperature.



To a suspension of either the *S*- or *O, O'*-sulfinato form of $[IrCl_2(SO_2CF_3)(PPh_3)_2]$ (0.1 g) in benzene (3 ml) was added 0.2 ml of pyridine. Ether (5 ml) was added to give a sticky precipitate. The liquid phase was decanted and the residue was triturated with ether to give a pale yellow solid. Yield 0.05 g.

Acknowledgement

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References

- 1 A. Wojcicki, *Advan. Organometal. Chem.*, **12** (1974) 32.
- 2 G. Vitzthum and E. Lindner, *Angew. Chem. Internat. Edit.*, **10** (1971) 315.
- 3 J. Blum and G. Scharf, *J. Org. Chem.*, **35** (1970) 1895.
- 4 S.E. Jacobsen, P. Reich-Rohrwig and A. Wojcicki, *Inorg. Chem.*, **12** (1973) 717.
- 5 J.P. Collman and W.R. Roper, *J. Amer. Chem. Soc.*, **88** (1966) 180.
- 6 S.P. Dent and C. Eaborn, *J. Organometal. Chem.*, **97** (1975) 307.
- 7 M. Kubota and B.M. Loeffler, *Inorg. Chem.*, **11** (1972) 469.
- 8 T.A. George and D.D. Watkins, Jr., *Inorg. Chem.*, **12** (1973) 398.
- 9 A.J. Deeming and B.L. Shaw, *J. Chem. Soc. (A)*, (1969) 1128.
- 10 C.A. Reed and W.R. Roper, *Chem. Commun.*, (1971) 1556.
- 11 T.G. Appleton, H.C. Clark and L.E. Manzer, *Coord. Chem. Rev.*, **10** (1973) 362.
- 12 D.M. Blake, A. Winkelman and Y.L. Chung, *Inorg. Chem.*, **14** (1975) 1326.
- 13 A.L. Balch and Y.S. Sohn, *J. Amer. Chem. Soc.*, **94** (1972) 1144.
- 14 A. Wojcicki, *Advan. Organometal. Chem.*, **11** (1973) 87.
- 15 M. Kubota, Private Communication.
- 16 J.P. Collman, C.T. Sears and M. Kubota, *Inorg. Syn.*, **XI** (1968) 102.
- 17 J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun and J.W. Kang, *J. Amer. Chem. Soc.*, **90** (1968) 5430.