and 2.52 (16) Å, respectively. The shift of O(3) affects the hydrogen bonding scheme. The hydrogen bond distances now are O(1)–O(2) = 2.77 (16) Å, O(2)–O(3) = 3.99(30) Å, and O(1)–O(3) = 3.30 (25) Å. Although the standard deviations are high, it is clear the hydrogen bonding scheme must be different from that for the Mn salt. The other bond distances for Co–C and C–N of 1.872 (15) and 1.16 (3) Å are in good agreement with $Cs_2LiCo(CN)_6$. All of these bond distances are given in Table II.

There are several interesting points about this new model. The first is that the divalent metal now has octahedral, or close to octahedral, coordination in contrast to the model of Ludi.[4] Second, the hydrogen bonding structure seems to be quite important in stabilizing the structure. The implications of these results in regard to semipermeability are quite intriguing. From this model it appears that there are four possible factors involved in the transport mechanism. The four factors are σ-bonding properties, hydrogen-bonding capability, neutral charge, and size. It appears that any molecule which is charged or which is larger than 7.0 Å cannot enter the lattice. The other two factors appear to be of approximately the same importance. The mechanism of transport through the lattice appears to involve initially hydrogen bond formation between O_1 and O_3. The second step in the transport must involve the breaking of the original hydrogen bond and re-formation of the hydrogen bond with a different O_1. This might be accomplished through a temporary hydrogen bond with O_2. It appears from bonding energy considerations that O_1 is not transported through the lattice but is essential for transport of other water molecules.

Some calculations on the ordered model proposed by Weiser, Milligan, and Bates[3] have been carried out to determine how this completely ordered model refines in comparison to the disordered model proposed in this work. The two models were refined employing 160, 76, and 24 reflections. The 24 reflections were chosen because that is approximately the amount of data that was available from powder data. In a refinement of 24 reflections the ordered model gives a better *R* value and more reasonable C–N and Co–C bond distances. The only problem with the ordered model in this refinement was that the temperature factor on the interstitial divalent metal (8c, $^1/_4$, $^1/_4$, $^1/_4$) was quite high. This fact would not have been noticed in 1942, since temperature factors were not commonly refined at that time. The refinements of the data with all the reflections (160) point out the superiority of the disordered structure.

Table V compares observed and calculated crystal structure factors.

Acknowledgment. J.K. and I.B. acknowledge support from National Science Foundation Grant No. MPS-74-13718 and The Robert A. Welch Foundation Grant No. E-594. G.W.B. and W.O.M. also wish to acknowledge the Robert A. Welch Foundation Grant No. AA-668. We wish to thank Dr. F. A. Cotton for the use of the Syntex $P\bar{1}$ diffractometer. Also, we thank the Department of Chemistry at Brookhaven National Laboratory for the use of the neutron diffraction facilities and Dr. R. K. McMullan for help during data collection at BNL.

Registry No. $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$, 63976-80-7; $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$, 23540-99-0.

Supplementary Material Available: Listings of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Research performed in part under auspicies of U.S. Energy Research and Development Administration.
(2) (a) Baylor University. (b) University of Houston. (c) Research Collaboration at Brookhaven National Laboratory, Oct–Nov 1975.
(3) H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **46**, 99–111 (1942).
(4) A. Ludi, H. U. Gudel, and M. Ruegg, *Inorg. Chem.*, **9**, 2224 (1970).
(5) V. G. Ron, A. Ludi, and P. Engel, *Chimia*, **27**, 77 (1973).
(6) A. Ludi and H. U. Gudel, *Helv. Chim. Acta*, **51**, 2006 (1968).
(7) F. A. Cotton, B. A. Fernz, G. Daganelto, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973).
(8) The absorption program used is a modification of the original by W. R. Busing and H. A. Levi.
(9) B. I. Swanson and R. R. Ryan, *Inorg. Chem.*, **12**, 283 (1973).
(10) A. C. Larson, *Acta Crystallogr.*, **23**, 664 (1967).
(11) All programs used in the refinements are from Los Alamos Scientific Laboratories Government Report No. LA-3043 (1964).
(12) D. T. Cromer and H. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(13) D. T. Cromer, *Acta Crystallogr.*, **18**, 17–23 (1965).
(14) B. I. Swanson, *Inorg. Chem.*, **15**, 253 (1976).
(15) G. Ferraris and M. Franchini-Angela, *Acta Crystallogr., Sect. B*, **28**, 3572 (1972).
(16) I. B. Brown, *Acta Crystallogr., Sect. A*, **32**, 24 (1976).

Contribution from the Department of Chemistry,
King's College, Strand, London, WC2R 2LS, England

Complexes of the Platinum Metals. 10.[1] Dithioformato Derivatives of Ruthenium, Osmium, and Iridium

STEPHEN D. ROBINSON* and ARVIND SAHAJPAL

Received January 24, 1977 AIC70063F

"Insertion" of carbon disulfide into platinum metal–hydrogen bonds has been employed to synthesize a range of new dithioformato complexes. Products prepared in this manner include the species $[MX(S_2CH)(CO)(PPh_3)_2]$ (two $[MX(RN{\doteq}CH{\doteq}S)(CO)(PPh_3)_2]$ M = Ru or Os; X = Cl, Br, or $OCOCF_3$), $[M(S_2CH)_2(PPh_3)_2]$, $[IrCl_2(S_2CH)(PPh_3)_2]$, $[MH(RN{\doteq}CH{\doteq}S)(CO)(PPh_3)_2]$, $[Ru(RN{\doteq}CH{\doteq}S)_2(PPh_3)_2]$, Phosphine substitution reactions have been employed to prepare the species $[MCl(S_2CH)(CO)(PMe_2Ph)_2]$ and $[MCl(S_2CH)(CO)(PMePh_2)_2]$. The stereochemistry of each new complex has been assigned by reference to the ^1H NMR spectrum of the dithioformate (S_2CH) ligands and has been confirmed where appropriate by use of high-field (metal hydride) resonances, virtual coupling patterns of the PMe_nPh_{3-n} (n = 1 or 2) ligands, or the ^{31}P NMR pattern of the phosphine ligands.

Introduction

Synthesis of the platinum carbon disulfide[2] and rhodium thiocarbonyl[3,4] complexes $[Pt(CS_2)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$, respectively, by Wilkinson et al. has stimulated much interest in the reactions of carbon disulfide with transition-metal species.[5] However, many of the products obtained are ill characterized, in particular their stereochemistry and structure are frequently not adequately established. We now find that the dithioformate anion, one of the ligands most commonly encountered in these systems,[5-8] can be detected and characterized by its IR and proton NMR spectra. Furthermore, couplings of the dithioformate central

Table I. Analytical[a] and Melting Point Data

Complex and stereochemistry	% C	% H	Mp/°C
$[RuCl(S_2CH)(CO)(PPh_3)_2]$ (II)	59.41 (59.56)	4.22 (4.08)	214–216
$[RuCl(S_2CH)(CO)(PPh_3)_2]$ (IV)	58.86 (59.56)[f]	4.23 (4.08)	216–218
$[RuBr(S_2CH)(CO)(PPh_3)_2]$ (II)	55.98 (56.30)	4.13 (3.85)	226–228
$[RuBr(S_2CH)(CO)(PPh_3)_2]$ (IV)	56.32 (56.30)	3.95 (3.85)	224–226
$[Ru(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$[b] (II)	57.0 (56.9)	3.7 (3.7)	174–176
$[Ru(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$[c] (IV)	56.5 (56.9)	3.7 (3.7)	194–195
$[OsCl(S_2CH)(CO)(PPh_3)_2]$ (II)	53.36 (53.36)	3.71 (3.65)	225–227
$[OsCl(S_2CH)(CO)(PPh_3)_2]$ (IV)	54.02 (53.36)[f]	3.60 (3.65)	227–229
$[OsBr(S_2CH)(CO)(PPh_3)_2]$ (II)	50.49 (50.72)	3.62 (3.47)	229–232
$[OsBr(S_2CH)(CO)(PPh_3)_2]$ (IV)	49.99 (50.72)[f]	3.50 (3.47)	228–231
$[Os(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$[d] (II)	51.5 (51.5)	3.0 (3.3)	199–200
$[RuCl(S_2CH)(CO)(PMe_2Ph)_2]$ (II)	41.60 (41.73)	4.46 (4.47)	135–138
$[RuCl(S_2CH)(CO)(PMe_2Ph)_2]$ (IV)	42.28 (41.73)	4.61 (4.47)	95–97
$[RuCl(S_2CH)(CO)(PMePh_2)_2]$ (IV)	50.77 (51.09)	4.16 (4.14)	148–150
$[OsCl(S_2CH)(CO)(PMe_2Ph)_2]$[e] (II)	35.75 (35.61)	3.94 (3.81)	144–146
$[OsCl(S_2CH)(CO)(PMePh_2)_2]$ (II)	45.98 (45.98)	3.76 (3.82)	145–147
$[Os(S_2CH)_2(PPh_3)_2]$ (V)	52.15 (52.5)	3.76 (3.7)	185–187
$[IrCl_2(S_2CH)(PPh_3)_2]$ (VII)	51.16 (51.38)	3.62 (3.61)	247–250
$[IrH_2(S_2CH)(PPh_3)_2]$ (IX)	54.97 (55.83)[f]	4.24 (4.2)	172–174

[a] Calculated figures given in parentheses. [b–e] Phosphorus analyses: *b*, 7.8 (7.6); *c*, 7.7 (7.6); *d*, 6.5 (6.6); *e*, 10.2 (10.28). [f] Poor carbon analyses due to traces of occluded solvent.

proton (S_2CH) to the adjacent hydride [$^4J(HH)$] and/or phosphorus donor atoms [$^4J(PH)$] are valuable sources of stereochemical information and frequently permit the assignment of complete stereochemistry. In order to confirm these observations we have synthesized and characterized the most extensive series of dithioformato complexes reported to date and, in several instances, have made independent stereochemical assignments based on high-field proton NMR patterns and/or NMR virtual coupling patterns of coordinated PMe_nPh_{3-n} ligands (n = 1 or 2). A preliminary note on this work has been published elsewhere.[9]

Experimental Section

Hydride complexes were prepared by standard literature procedures,[10] reagent grade carbon disulfide and organic solvents were used as purchased. Reactions were performed under nitrogen but products were worked up in air. Unless otherwise indicated, products were purified by washing successively with methanol and light petroleum (bp 60–80 °C), recrystallizing from dichloromethane–methanol and then drying in vacuo. Yields are based on platinum metal content and, where given in percentage terms alone, refer to syntheses performed on a ca. 0.5-mmol scale. 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 ^{31}P NMR spectra were taken at 90 and 36.43 MHz, respectively, using a Bruker HFX90 spectrometer. Infrared spectra were obtained for Nujol mulls using a Perkin-Elmer 457 grating spectrometer. Spectroscopic data are given in Table II.

Carbonylchloro(dithioformato)bis(triphenylphosphine)ruthenium(II)—Stereochemistry II. Carbon disulfide (10 mL) was added to carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.34 g) in benzene (20 mL) and the mixture heated under reflux for ca. 30 min to give a yellow solution. The solution was cooled to ambient temperature and filtered and then concentrated under reduced pressure and diluted with methanol (10 mL) to precipitate the product as a yellow solid. This was purified as described above to give bright yellow crystals (0.22 g, 85%).

Carbonylchloro(dithioformato)bis(triphenylphosphine)ruthenium(II)—Stereochemistry IV. This isomer was similarly prepared by heating a mixture of carbon disulfide (10 mL) and carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.34 g) in toluene (20 mL) under reflux for 3 h and was crystallized from dichloromethane–methanol as bright yellow crystals (0.23 g, 88%).

Bromocarbonyl(dithioformato)bis(triphenylphosphine)ruthenium(II)—Stereochemistry II. Carbon disulfide (10 mL) and bromocarbonylhydridotris(triphenylphosphine)ruthenium (0.3 g) in benzene (20 mL) were heated under reflux for ca. 5 min. The resultant yellow solution was cooled to room temperature, filtered, concentrated under reduced pressure, and then diluted with methanol (10 mL) to yield the product as a yellow solid. This was purified and crystallized as described above to give yellow crystals (0.2 g, 74%).

Bromocarbonyl(dithioformato)bis(triphenylphosphine)ruthenium(II)—stereochemistry IV was similarly prepared by heating a mixture of carbon disulfide (10 mL) and bromocarbonylhydridotris(triphenylphosphine)ruthenium (0.36 g) under reflux in benzene for ca. 30 min and was purified as described above to yield yellow microcrystals (0.21 g, 78%).

Carbonyl(trifluoroacetato)dithioformatobis(triphenylphosphine)ruthenium(II)—Stereochemistry II. Carbon disulfide (1 mL) and carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) were shaken together in cold benzene (5 mL) for 10 min. The resultant yellow solution was diluted with light petroleum and then left to crystallize. The large yellow crystals were washed successively with a minimum volume of methanol and light petroleum and then dried in vacuo; yield (0.18 g, 73%).

Carbonyl(trifluoroacetato)dithioformatobis(triphenylphosphine)ruthenium(II)—Stereochemistry IV. Carbon disulfide (5 mL) and carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) in benzene (10 mL) were heated under reflux for ca. 10 min. The resultant deep orange solution was evaporated under reduced pressure and the oil crystallized from dichloromethane–light petroleum as orange-brown crystals. These were filtered off, washed successively with a minimum volume of methanol and light petroleum, and then dried in vacuo; yield (0.17 g, 69%).

Carbonylchloro(dithioformato)bis(triphenylphosphine)osmium(II)—Stereochemistry II. Carbon disulfide (10 mL) was added to carbonylchlorohydridotris(triphenylphosphine)osmium (0.3 g) in toluene (20 mL) and the mixture heated under reflux for ca. 3 h. The resultant yellow solution was cooled to ambient temperature, filtered, then evaporated to small volume under reduced pressure, and finally diluted with methanol (10 mL) to precipitate a bright yellow powder. This was purified and crystallized as described above to yield yellow crystals (0.21 g, 74%).

Carbonylchloro(dithioformato)bis(triphenylphosphine)osmium(II)—stereochemistry IV was similarly prepared by heating carbon disulfide (10 mL) and carbonylchlorohydridotris(triphenylphosphine)osmium (0.3 g) under reflux in toluene (20 mL) for ca. 72 h. Recrystallization from dichloromethane–methanol gave the required product as yellow crystals (0.22 g, 77%) contaminated by traces of isomer II.

Bromocarbonyl(dithioformato)bis(triphenylphosphine)osmium(II)—Stereochemistry II. Carbon disulfide (10 mL) was added to bromocarbonylhydridotris(triphenylphosphine)osmium (0.36 g) in benzene (20 mL) and the mixture heated under reflux for ca. 1 h to give a brownish yellow solution which was cooled to ambient temperature and filtered. The filtrate was concentrated under reduced pressure and then diluted with methanol (10 mL) to precipitate a yellow solid. The precipitate was purified and crystallized as described above to yield yellow crystals (0.2 g, 67%).

Bromocarbonyl(dithioformato)bis(triphenylphosphine)osmium(II)—stereochemistry IV was similarly prepared by heating a mixture of carbon disulfide (10 mL) and bromocarbonylhydridotris(triphenylphosphine)osmium (0.36 g) under reflux in toluene (20 mL)

Table II. Infrared,[a] ^{31}P NMR,[b] and ^{1}H NMR[c] Data

Complex and stereochemistry	$\nu(S_2CH)$, cm^{-1}	ν(CO), cm^{-1}	^{31}P NMR δ, ppm	τ(CH)	^4J-(PH)$_{trans}$, Hz	^4J-(PH)$_{cis}$, Hz	Additional ^{1}H NMR data
$[RuCl(S_2CH)(CO)(PPh_3)_2]$ (II)	1230 w, 920 s	1958	36.12 s	−1.87 t	8.0	–	
$[RuCl(S_2CH)(CO)(PPh_3)_2]$ (IV)	1225, 1220 vw, 930 s	1950	33.46 s	−0.25 t	–	3.0	
$[RuBr(S_2CH)(CO)(PPh_3)_2]$ (II)	1235 w, 925 s	1950	35.18 s	−1.70 t	8.0	–	
$[RuBr(S_2CH)(CO)(PPh_3)_2]$ (IV)	1225 w, 925 s	1947		−0.15 t	–	3.0	
$[Ru(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$ (II)	1234 w, 930 s	1976		−1.85 t	7.1	–	
$[Ru(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$ (IV)	1228 w, 930 s	1970		+0.05 t		2.75	
$[OsCl(S_2CH)(CO)(PPh_3)_2]$ (II)	1235 w, 920 s	1932	−3.35 s	−3.65 t	8.0	–	
$[OsCl(S_2CH)(CO)(PPh_3)_2]$ (IV)	1235 w, 920 s	1930		−1.85 t	–	3.0	
$[OsBr(S_2CH)(CO)(PPh_3)_2]$ (II)	1230 w, 920 s	1935	−5.16 s	−3.45 t	8.5	–	
$[OsBr(S_2CH)(CO)(PPh_3)_2]$ (IV)	1222 vw, 920 s	1930	−1.76 s	−1.90 t	–	3.0	
$[Os(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$ (II)	1230 w, 925 s	1960		−3.58 t	8.25	–	
$[RuCl(S_2CH)(CO)(PMe_2Ph)_2]$ (II)	1235 w, 930 s	1950		−2.07 t	7.5	–	τ(Me) 8.34 not resolved
$[RuCl(S_2CH)(CO)(PMe_2Ph)_2]$ (IV)	1240 w, 928 s	1935		−1.05 t	–	3.7	τ(Me) 8.08 pt, 8.14 pt; $\lvert{}^2J(PH) + {}^4J(PH)\rvert = 7$ Hz
$[RuCl(S_2CH)(CO)(PMePh_2)_2]$ (IV)	1235 w, 928 s	1940		−0.5 t		3.5	τ(Me) 7.80 pt, $\lvert{}^2J(PH) + {}^4J(PH)\rvert = 7$ Hz
$[OsCl(S_2CH)(CO)(PMe_2Ph)_2]$ (II)	1235 w, 922 s	1927		−3.84 t	7.7	–	τ(Me) 8.22 d, 8.25 d; $^2J(PH) = 9.2$ Hz
$[OsCl(S_2CH)(CO)(PMePh_2)_2]$ (II)	1240 w, 930 s	1927		−3.78 t	7.8	–	τ(Me) 7.98 d; $^2J(PH) = 9.2$ Hz
$[Os(S_2CH)_2(PPh_3)_2]$ (V)	1220, 1215 w, 910, 902 s		−4.83 s	−3.24 d	5.5	$\simeq 0$	
$[IrCl_2(S_2CH)(PPh_3)_2]$ (VII)	1230 w, 915 s		−24.86 s	−3.20 t	10.0	–	
$[IrH_2(S_2CH)(PPh_3)_2]$ (IX)	1235 w, 930 s	2170, 2080[d]	18.83 s	−3.37 t		3.0	τ(IrH) 29.93; $^2J(PH)_{cis} = 17$ Hz, $^4J(HH')_{trans} = 15$ Hz

[a] Taken as Nujol mulls. Key: w = weak, s = strong. [b] Taken in $CDCl_3$ solution and referenced to external H_3PO_4 in the sense that positive values are to low field. All spectra are proton decoupled; s = singlet. [c] Taken in $CDCl_3$ solution and referenced to internal Me_4Si; d = doublet, t = triplet, pt = pseudo triplet. [d] ν(IrH), cm^{-1}.

for ca. 8 h. The product was obtained as orange crystals (0.26 g, 87%).

Carbonyl(trifluoroacetato)dithioformatobis(triphenylphosphine)osmium(II)—Stereochemistry II. Carbon disulfide (5 mL) and carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)osmium (0.25 g) in benzene (10 mL) were heated under reflux for 20 min. The yellow-orange solution was cooled to room temperature, filtered, and concentrated under reduced pressure and the residue purified and crystallized as described above to yield dark orange-brown crystals (0.19 g, 68%).

Carbonylchloro(dithioformato)bis(dimethylphenylphosphine)ruthenium(II)—Stereochemistry II. Dimethylphenylphosphine (0.05 g) was added to carbonylchloro(dithioformato)bis(triphenylphosphine)ruthenium (stereochemistry II) (0.4 g) and the mixture heated under reflux for ca. 10 min to give a yellow-orange solution which was successively cooled, filtered, and concentrated under reduced pressure. The residual oil was dissolved in the minimum quantity of dichloromethane and then diluted with light petroleum and allowed to crystallize at 0 °C. The product was then purified and recrystallized as described above but using light petroleum in place of methanol to yield yellow microcrystals (0.13 g, 76%).

Similarly prepared using the appropriate phosphine were carbonylchloro(dithioformato)bis(dimethylphenylphosphine)ruthenium(II)—stereochemistry IV as orange crystals (82%), carbonylchloro(dithioformato)bis(methyldiphenylphosphine)ruthenium(II)—stereochemistry IV as yellow microcrystals (74%), carbonylchloro(dithioformato)bis(dimethylphenylphosphine)osmium(II)—stereochemistry II as feathery orange needles (77%), and carbonylchloro(dithioformato)bis(methyldiphenylphosphine)osmium(II)–stereochemistry II as yellow crystals (67%).

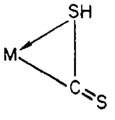
Bis(dithioformato)bis(triphenylphosphine)osmium(II). Carbon disulfide (10 mL) and tetrahydridotris(triphenylphosphine)osmium (0.33 g) in benzene (20 mL) were heated under reflux for ca. 3 h. The dark red solution was cooled to ambient temperature, filtered, and then evaporated under reduced pressure to give a dark red solid. This was purified and crystallized as described above to yield shiny dark red crystals (0.22 g, 76%).

Dichloro(dithioformato)bis(triphenylphosphine)iridium(III). Carbon disulfide (10 mL) was added to *trans*-dichlorohydridotris(triphenylphosphine)iridium (0.35 g) in benzene (20 mL) and the mixture was heated under reflux for ca. 30 min. The dark yellow-green solution was cooled to room temperature, filtered, and concentrated to small volume under reduced pressure and then diluted with methanol (10 mL) to precipitate the product as a yellow powder. The precipitate was purified and crystallized as described above to yield bright yellow microcrystals (0.18 g, 64%).

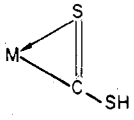
Dihydrido(dithioformato)bis(triphenylphosphine)iridium(III). *mer*-Trihydridotris(triphenylphosphine)iridium (0.17 g) was suspended in benzene (20 mL) and carbon disulfide (10 mL). The mixture was heated under reflux for ca. 2 h to form a bright yellow solution which was cooled to ambient temperature and filtered. The filtrate was concentrated to a volume of ca. 2–3 mL under reduced pressure and then diluted with methanol to precipitate the product as a yellow solid. The precipitate was purified and crystallized as described above to yield yellow crystals (0.16 g, 61%).

Results and Discussion

Data discussed below for the ruthenium–, osmium–, and iridium–dithioformato complexes clearly establish that the proton resonance of the dithioformate (S_2CH) ligand occurs at very low field (ca. τ 0.5 to −4.0 in the present complexes) and that the NMR couplings of the dithioformate proton to neighboring hydride [$^4J(HH)$] and phosphorus donor ligands [$^4J(PH)$] are a valuable source of stereochemical information. In particular, the coupling of the dithioformate proton (S_2CH) to a trans phosphorus nucleus [$^4J(PH)_{trans}$ = ca. 5.5–10 Hz] is substantially greater than to a cis phosphorus nucleus [$^4J(PH)_{cis}$ = ca. 0–3 Hz]. Furthermore, equivalent coupling of the dithioformate proton to pairs of ^{31}P nuclei in many of the complexes studied here (vide infra) clearly confirms the symmetrical structure shown for the dithioformate ligands in this paper and established by x-ray diffraction methods for $[Ru(S_2CH)_2(PPh_3)_2]$[11] and $[Re(S_2CH)(CO)_2(PPh_3)_2]$.[12] The alternative asymmetric structures (Ia and b) are excluded by virtue of the same data.



Ia



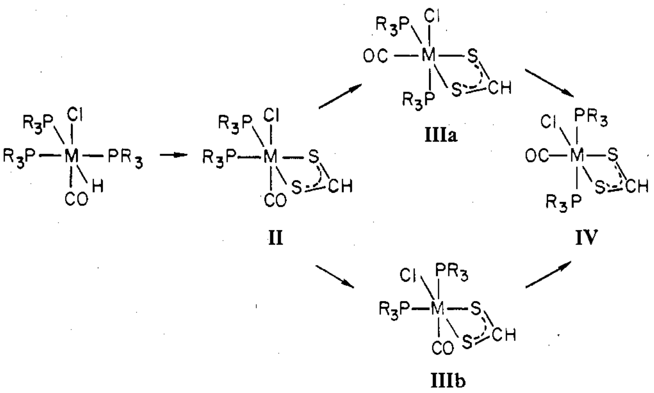
Ib

The infrared spectra of the new complexes are also in accord with the presence of dithioformate ligands. The dithioformate ion, as its potassium salt ($K^+S_2CH^-$), shows infrared-active bands at ca. 1250, 980, and 786 cm^{-1} attributable to δ(HCS), $\nu(CS_2)_{asym}$, and $\nu(CS_2)_{sym}$, respectively.[13] For chelate dithioformate ligands the same vibrations are thought to occur at ca. 1245, 1000–980, and 780 cm^{-1}, respectively.[5,8] The dithioformato complexes described in the present paper show the expected infrared bands at ca. 1240–1220 and 930–900 cm^{-1} attributable to δ(HCS) and $\nu(CS_2)_{asym}$, respectively. However, the region 800–700 cm^{-1} is partially masked by vibrations associated with the phosphine ligands, and we are unable to make a positive assignment for $\nu(CS_2)_{sym}$. Finally, the absence of bands attributable to ν(SH) is further evidence against the presence of the asymmetric structures (Ia and b).

Complexes $[MX(S_2CH)(CO)(PR_3)_2]$ (M = Ru or Os; X = Cl, Br, or $OCOCF_3$; R_3 = Ph_3, Ph_2Me, or $PhMe_2$). The hydrides $[MHX(CO)(PPh_3)_3]$ react with carbon disulfide in boiling benzene to yield the products $[MX(S_2CH)(CO)(PPh_3)_2]$ (II) as air-stable yellow crystalline solids. On further heating in benzene or toluene solution many of these products form isomers, IV. The ease of isomerization decreases in the order Ru > Os and Br > Cl $\approx$ $OCOCF_3$; thus when M = Os and X = Cl or $OCOCF_3$ the pure isomer IV could only be obtained by exhaustive treatment. The dithioformates $[MX(S_2CH)(CO)(PPh_3)_2]$ undergo phosphine exchange when heated with PMe_2Ph or $PMePh_2$ to afford the products $[MCl(S_2CH)(CO)(PMe_2Ph)_2]$ (II, M = Ru or Os; IV, M = Ru) or $[MCl(S_2CH)(CO)(PMePh_2)_2]$ (II, M = Os; IV, M = Ru). The isomerization process (II → IV) is thought to involve an intermediate isomer (IIIa or b) in each instance. Experimental evidence for the formation of an intermediate isomer has not been obtained in the present work on carbon disulfide insertion. However, analogous intermediates are observed during the reactions of isothiocyanates (RN=C=S)[14] and carbodiimides (RN=C=NR)[15] with the hydrides $[MHX(CO)(PPh_3)_3]$, and it seems probable that all three classes of substrate, S=C=S, RN=C=S, and RN=C=NR follow the same pathway. Our failure to detect the intermediate isomer (IIIa or b) in any of the present reactions presumably indicates that the second isomerization step is at least as rapid as the first.

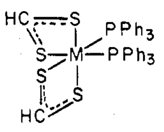
The stereochemistry of the products II and IV can be readily assigned by reference to the proton NMR pattern of the dithioformate (S_2CH) ligand which occurs as a multiplet in the region τ 0.5 to −4.0. Thus the products $[MX(S_2CH)(CO)(PPh_3)_2]$ formed under mild conditions show low-field proton NMR triplets $[^4J(PH)_{trans}$ = ca. 8 Hz] indicative of stereochemistry II. The isomeric species $[MX(S_2CH)(CO)(PPh_3)_2]$, obtained using more vigorous conditions and/or longer reaction times, display low-field triplets $[^4J(PH)_{cis}$ = ca. 3 Hz] consistent with stereochemistry IV. These assignments are in accord with the reaction sequence shown in Scheme I. Confirmation of the stereochemical assignments II and IV is provided by the ^1H and ^{31}P NMR spectra of the phosphine ligands. The methyl resonances for isomers of stereochemistry II (PR_3 = PMe_2Ph) each comprise two virtual coupling doublets indicative of an equivalent pair of mutually cis PMe_2Ph ligands each bearing a pair of nonequivalent methyl groups. The corresponding resonance for the methyl groups in products of stereochemistry IV (PR_3 = PMe_2Ph) comprises a pair of overlapping virtual coupling triplets indicative of two equivalent mutually trans phosphine ligands each bearing two nonequivalent methyl groups. At 220 MHz these triplets are fully resolved. The methyl protons of the complexes $[MX(S_2CH)(CO)(PMePh_2)_2]$ (isomers II and IV) give rise to virtual coupling doublet and triplet patterns, respectively. In each instance the proton-decoupled ^{31}P NMR spectrum of the isomers II and IV consists of a singlet. Related complexes $[MX(S_2CH)(CO)(PR_3)_2]$ (R = C_6H_{11}) have been reported by other workers;[6] however, NMR data for the thioformate ligands were not recorded and stereochemical assignments were not rigorously established.

Scheme I

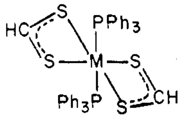


R_3 = Ph_3, Ph_2Me, or $PhMe_2$

Complexes *cis*-$[M(S_2CH)_2(PPh_3)_2]$ (M = Ru or Os). These products were obtained by treating $[RuH_2(PPh_3)_4]$ with neat carbon disulfide and by treating $[OsH_4(PPh_3)_3]$ with carbon disulfide in boiling benzene. The ruthenium complex $[Ru(S_2CH)_2(PPh_3)_2]$ has previously been prepared[16] and shown by x-ray diffraction methods[11] to possess stereochemistry V (M = Ru). By analogy the new osmium complex $[Os(S_2CH)_2(PPh_3)_2]$ is assigned similar stereochemistry. In each instance the proton NMR spectrum of the dithioformate ligands comprises a narrow doublet pattern. Although the couplings $[^4J(PH)_{trans}]$ and $[^4J(PH)_{cis}]$ at ca. 1.5–5.5 Hz and ca. 0.0 Hz, respectively, are significantly less than those found for complexes of types II and IV, the multiplicity of the pattern clearly favors stereochemistry V rather than the alternative VI. For the latter stereochemistry either a singlet $[^4J(PH)_{cis}$ $\approx$ 0.0 Hz] or a triplet $[^4J(PH)_{cis}$ > 0.0 Hz] signal would be expected.

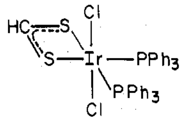


V

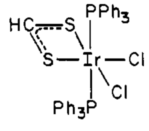


VI

Complexes $[IrCl_2(S_2CH)(PPh_3)_2]$ and $[IrH_2(S_2CH)(PPh_3)_2]$. The reaction of $[IrHCl_2(PPh_3)_3]$ (trans chlorides) with carbon disulfide in boiling benzene affords the yellow air-stable crystalline solid $[IrCl_2(S_2CH)(PPh_3)_2]$. The triplet pattern observed for the dithioformate proton demonstrates the presence of equivalent phosphine ligands and the magnitude of the coupling constant $[^4J(PH)$ = 10 Hz] indicates that they are both trans to the dithioformate ligand. The complex can therefore be assigned stereochemistry VII. Attempts to achieve the isomerization VII → VIII, analogous to that observed with the corresponding thioformamide derivatives,[14] were unsuc-

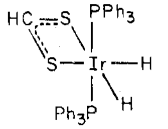


VII



VIII

cessful, presumably because of the greater inertness of the Ir–S bond relative to the Ir–N linkage. Treatment of *mer*-$[IrH_3(PPh_3)_3]$ with carbon disulfide in boiling benzene afforded the yellow air-stable dihydrido complex $[IrH_2(S_2CH)(PPh_3)_2]$ which displayed no tendency to react further with carbon disulfide. The proton NMR spectrum of the dithioformate ligand comprises a triplet indicative of two equivalent phosphine ligands, and the relatively small magnitude of the coupling $[{}^4J(PH)_{cis} = \text{ca. } 3\ Hz]$ establishes the stereochemistry IX. The high-field proton resonance $[\tau(IrH)\ 29.93;\ {}^2J(PH)_{cis} = 17\ Hz]$ confirms this assignment. Proton–proton NMR coupling between the hydride and dithioformate ligands $[{}^4J(HH')_{trans} = 1.5\ Hz]$ is also observed.



IX

Mechanistic studies of the individual syntheses described in this paper and the two following papers are in progress and will be reported elsewhere.

Acknowledgment. We thank Dr. D. A. Couch for obtaining NMR spectra, Johnson Matthey and Co., Ltd., for loan of platinum metals, and the British Council for financial aid to A.S.

Registry No. $[RuCl(S_2CH)(CO)(PPh_3)_2]$(II), 58410-58-5; $[RuCl(S_2CH)(CO)(PPh_3)_2]$(IV), 58437-76-6; $[RuBr(S_2CH)(CO)(PPh_3)_2]$(II), 58410-59-6; $[RuBr(S_2CH)(CO)(PPh_3)_2]$(IV), 58437-77-7; $[Ru(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$(II), 63701-13-3; $[Ru(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$(IV), 58410-62-1; $[OsCl(S_2CH)(CO)(PPh_3)_2]$(II), 58410-60-9; $[OsCl(S_2CH)(CO)(PPh_3)_2]$(IV), 58437-78-8; $[OsBr(S_2CH)(CO)(PPh_3)_2]$(II), 58410-61-0; $[OsBr(S_2CH)(CO)(PPh_3)_2]$(IV), 58437-79-9; $[Os(OCOCF_3)(S_2CH)(CO)(PPh_3)_2]$(II), 58410-63-2; $[RuCl(S_2CH)(CO)(PMe_2Ph)_2]$(II), 63658-27-5; $[RuCl(S_2CH)(CO)(PMe_2Ph)_2]$(IV), 63701-14-4; $[RuCl(S_2CH)(CO)(PMePh_2)_2]$(IV), 63658-28-6; $[OsCl(S_2CH)(CO)(PMe_2Ph)_2]$(II), 63658-29-7; $[OsCl(S_2CH)(CO)(PMePh_2)_2]$(II), 63658-30-0; $[Os(S_2CH)_2(PPh_3)_2]$(V), 58410-79-0; $[IrCl_2(S_2CH)(PPh_3)_2]$(VII), 58410-73-4; $[IrH_2(S_2CH)(PPh_3)_2]$(IX), 58452-21-4; $[RuHCl(CO)(PPh_3)_3]$, 16971-33-8; $[RuHBr(CO)(PPh_3)_3]$, 16971-34-9; $[RuH(OCOCF_3)(CO)(PPh_3)_2]$, 63701-15-5; $[OsHCl(CO)(PPh_3)_3]$, 16971-31-6; $[OsHBr(CO)(PPh_3)_3]$, 16971-32-7; $[OsH(OCOCF_3)(CO)(PPh_3)_2]$, 63701-16-6; $[OsH_4(PPh_3)_3]$, 24228-59-9; *trans*-$[IrHCl_2(PPh_3)_3]$, 28060-70-0; *mer*-$[IrH_3(PPh_3)_3]$, 18660-47-4; CS_2, 75-15-0.

References and Notes

(1) Part 9: A. Dobson and S. D. Robinson, *Inorg. Chem.*, **16**, 1321 (1977).
(2) M. C. Baird and G. Wilkinson, *Chem. Commun.*, 514 (1966); *J. Chem. Soc. A*, 865 (1967).
(3) M. C. Baird and G. Wilkinson, *Chem. Commun.*, 267 (1966).
(4) M. C. Baird, G. Hartwell, and G. Wilkinson, *J. Chem. Soc. A*, 2037 (1967).
(5) For a recent review of this field see I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, **66**, 161 (1974).
(6) F. G. Moers, R. W. M. ten Hoedt, and J. P. Langhout, *Inorg. Chem.*, **12**, 2196 (1973); *J. Organomet. Chem.*, **65**, 93 (1974).
(7) A. Albinati, A. Musco, G. Carturan, and G. Strukul, *Inorg. Chim. Acta*, **18**, 219 (1976).
(8) F. W. Einstein, E. Enwall, N. Flitcroft, and J. M. Leach, *J. Inorg. Nucl. Chem.*, **34**, 885 (1972).
(9) S. D. Robinson and A. Sahajpal, *J. Organomet. Chem.*, **99**, C65 (1975).
(10) N. Ahmad, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 843 (1972).
(11) A. E. Kalinin, A. I. Gusev, and Y. T. Struchkov, *J. Struct. Chem.* (*Engl. Transl.*), **14**, 804 (1973).
(12) V. G. Albano, P. L. Bellon, and G. Ciani, *J. Organomet. Chem.*, **31**, 75 (1971).
(13) R. Mattes and W. Stork, *Spectrochim. Acta, Part A*, **30a**, 1385 (1974).
(14) S. D. Robinson and A. Sahajpal *Inorg. Chem.*, **16**, 2722 (1977).
(15) L. D. Brown, J. A. Ibers, S. D. Robinson and A. Sahajpal, *Inorg. Chem.*, **16**, 2728 (1977).
(16) R. O. Harris, N. K. Hota, L. Sadavoy, and J. M. C. Yuen, *J. Organomet. Chem.*, **54**, 259 (1973).

Contribution from the Department of Chemistry,
King's College, Strand, London WC2R 2LS, England

Complexes of the Platinum Metals. 11.[1] *N*-Alkyl- and *N*-Arylthioformamido Derivatives of Ruthenium, Osmium, and Iridium

STEPHEN D. ROBINSON* and ARVIND SAHAJPAL

Received February 25, 1977 AIC701454

Alkyl and aryl isothiocyanates (RNCS, R = Me, Et, Ph, or *p*-tolyl) undergo "insertion" reactions with platinum metal hydrides to yield products containing the corresponding *N*-alkyl- or *N*-arylthioformamide ligands ($RN\overset{\cdots}{-}CH\overset{\cdots}{-}S$). Complexes prepared in this manner or characterized in solution include $[MX(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)(CO)(PPh_3)_2]$ (three isomers; M = Ru or Os; X = Cl, Br, or $OCOCF_3$), $[MH(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)(CO)(PPh_3)_2]$, $[Ru(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)_2(PPh_3)_2]$, and $[IrCl_2(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)(PPh_3)_2]$ (two isomers). The structure of the *N*-alkyl- and *N*-arylthioformamide ligands and the stereochemistry of the complexes have been established using infrared and proton or phosphorus-31 NMR spectroscopy.

Although the reactions of carbon disulfide with transition-metal complexes have been extensively investigated,[2] relatively little is known concerning the corresponding behavior of alkyl and aryl isothiocyanates.[3] Transition-metal isothiocyanate derivatives previously reported include S- or C,S-bonded rhodium(III) and platinum(II) species[4] and two novel rhodium(III) complexes, one containing a tridentate O,C,S-bonded carbene ligand formed by condensing two benzoyl isothiocyanate moieties[5] and the other containing a tridentate S,C,S-bonded carbene ligand derived from three ethoxycarbonyl isothiocyanate molecules.[6] Insertion of isothiocyanates into metal–dimethylamido, metal–methyl, and metal–benzyl bonds affords group 4A or 5A metal complexes containing thioureide $[RN\overset{\cdots}{-}C(NMe_2)\overset{\cdots}{-}S]$,[7,8] thioacetamide $[RN\overset{\cdots}{-}C(Me)\overset{\cdots}{-}S]$,[8,9] and thiobenzamide $[RN\overset{\cdots}{-}C(Bz)\overset{\cdots}{-}S]$[10] ligands, respectively. However, the reactions of isothiocyanates with metal hydrides do not appear to have been investigated although the formation of dithioformates by insertion of carbon disulfide into transition-metal–hydrogen bonds is a well-established synthetic procedure.[1,2]

We now find that alkyl and aryl isothiocyanates parallel carbon disulfide in their ability to insert into metal–hydrogen bonds and that the products contain the novel *N*-alkyl- or *N*-arylthioformamide ($RN\overset{\cdots}{-}CH\overset{\cdots}{-}S$) chelate ligands. The stereochemistry of the new complexes and the bidentate