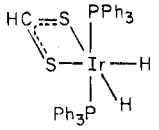
cessful, presumably because of the greater inertness of the Ir–S bond relative to the Ir–N linkage. Treatment of *mer*-$[IrH_3(PPh_3)_3]$ with carbon disulfide in boiling benzene afforded the yellow air-stable dihydrido complex $[IrH_2(S_2CH)(PPh_3)_2]$ which displayed no tendency to react further with 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 [$^4J(PH)_{cis}$ = ca. 3 Hz] establishes the stereochemistry IX. The high-field proton resonance [τ(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.

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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.

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

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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=CH=S). Complexes prepared in this manner or characterized in solution include $[MX(RN{=}CH{=}S)(CO)(PPh_3)_2]$ (three isomers; M = Ru or Os; X = Cl, Br, or $OCOCF_3$), $[MH(RN{=}CH{=}S)(CO)(PPh_3)_2]$, $[Ru(RN{=}CH{=}S)_2(PPh_3)_2]$, and $[IrCl_2(RN{=}CH{=}S)(PPh_3)_2]$ (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 $[RN{=}C(NMe_2){=}S]$,[7,8] thioacetamide $[RN{=}C(Me){=}S]$,[8,9] and thiobenzamide $[RN{=}C(Bz){=}S]$[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=CH=S) chelate ligands. The stereochemistry of the new complexes and the bidentate

Table I. Analytical[a] and Melting Point Data

Complex and stereochemistry	R	% C	% H	% N	% S	Mp/°C
[RuCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	63.8 (64.03)	4.56 (4.4)	1.78 (1.7)	4.25 (3.88)	226–229
[RuCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	*p*-tol	64.4 (64.4)	4.61 (4.56)	1.67 (1.7)	4.13 (3.82)	217–220
[RuCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Et	61.98 (61.8)	4.72 (4.67)	1.86 (1.8)	4.38 (4.13)	218–221
[RuBr(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	60.25 (60.8)	4.12 (4.17)	1.49 (1.61)	3.77 (3.7)	230–232
[Ru($OCOCF_3$)(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	61.27 (60.9)	4.06 (4.2)	1.63 (1.6)	3.82 (3.6)	205–208
[RuH(RN=CH=S)(CO)(PPh_3)$_2$] (IX)	Ph	66.05 (66.82)	4.72 (4.72)	1.87 (1.77)	4.45 (4.05)	201–203
[Ru(RN=CH=S)$_2$(PPh_3)$_2$][b] (XI)	Ph	65.68 (65.45)	4.63 (4.61)	3.16 (3.05)	7.22 (6.99)	170–173
[Ru(RN=CH=S)$_2$(PPh_3)$_2$] (XI)	Me	61.26 (62.01)	4.99 (4.94)	3.57 (3.62)	8.8 (8.3)	178–181
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Ph	57.6 (57.8)	4.06 (3.96)	1.5 (1.53)	3.17 (3.51)	232–234
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	*p*-tol	58.4 (58.23)	4.21 (4.13)	1.36 (1.51)	3.53 (3.5)	185–188
[OsBr(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Ph	54.96 (55.11)	3.79 (3.8)	1.46 (1.46)	3.98 (3.34)	233–236
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Me	55.95 (54.95)	4.38 (4.02)	1.83 (1.64)	3.39 (3.8)	262–266
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Et	54.7 (55.45)	4.24 (4.2)	1.59 (1.6)	3.37 (3.71)	228–230
[Os($OCOCF_3$)(RN=CH=S)(CO)(PPh_3)$_2$][c] (VI)	Ph	52.22 (52.53)	3.62 (3.45)	1.83 (1.33)	5.95 (5.89)[e]	185–187
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	57.51 (57.8)	3.97 (3.96)	1.54 (1.53)	6.75 (6.77)[e]	252–255
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	*p*-tol	58.35 (58.23)	4.23 (4.13)	1.43 (1.51)	3.38 (3.53)	226–229
[OsBr(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	54.66 (55.11)	3.66 (3.8)	1.42 (1.46)	3.15 (3.34)	236–239
[OsH(RN=CH=S)(CO)(PPh_3)$_2$][d] (IX)	Ph	56.83 (57.22)	4.09 (4.03)	1.59 (1.52)	3.16 (3.47)	237–239
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XII)	Me	53.24 (52.96)	4.08 (3.98)	1.66 (1.63)	3.77 (3.72)	252–255
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XII)	Et	53.05 (53.48)	4.10 (4.14)	1.37 (1.60)		254–256
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XIV)	Et	52.62 (53.48)	4.11 (4.14)	1.49 (1.60)	3.38 (3.66)	219–222
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XIV)	Ph	55.78 (55.9)	3.99 (3.93)	1.55 (1.52)	3.67 (3.47)	240–243
[$IrBr_2$(RN=CH=S)(PPh_3)$_2$] (XIV)	Ph	50.73 (50.99)	3.63 (3.6)	1.5 (1.4)	3.35 (3.7)	224–226

[a] Calculated figures given in parentheses. [b] Figures calculated for 4/1 benzene solvate. [c] Figures calculated for 2/1 chloroform solvate. [d] Figures calculated for 4/3 acetone solvate. [e] Phosphorus analyses.

Table II. Infrared and Proton NMR Data

Complex and stereochemistry	R	ν-(CO), cm^{-1}	ν-(MH), cm^{-1}	τ(CH)[a]	^4J-$(PH)_{trans}$, Hz	^4J-$(PH)_{cis}$, Hz	Other NMR resonances
[RuCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	1918		1.82 t		2.5	
[RuCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	*p*-tolyl	1920		1.92 t		2.8	τ(Me) 7.82 s
[RuCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Et	1920		Masked			$\tau(CH_2)$ 8.15 q, τ(Me) 10.06 t
[RuBr(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	1922		1.83 t		2.5	
[RuH(RN=CH=S)(CO)(PPh_3)$_2$] (IX)	Ph	1920	1974	1.49 t		2.8	τ(RuH) 21.9, $^2J(PH)_{cis}$ = 19 Hz
[Ru(RN=CH=S)$_2$(PPh_3)$_2$][b] (XI)	Ph			1.14 d	2.5		
[Ru(RN=CH=S)$_2$(PPh_3)$_2$] (XI)	Me			1.30 d	3.0		τ(Me) 7.65 s
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Ph	1920		0.5 d of d	8.0/2.0		
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	*p*-tolyl	1930		0.24 d of d	8.5/2.5		τ(Me) 7.72 s
[OsBr(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Ph	1920		0.26 d of d	9.0/3.0		
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Me	1930		−0.42 d of d	8.5/3.5		τ(Me) 7.63 d, ^4J(PH) = 1.5 Hz
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VI)	Et	1938		−0.51 d of d	8.8/3.5		
[Os($OCOCF_3$)(RN=CH=S)(CO)(PPh_3)$_2$][c] (VI)	Ph	1947		−0.05 d of d	8.2/1.45		
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	1900		0.65 t		2.5	
[OsCl(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	*p*-tolyl	1902		0.78 t		2.65	τ(Me) 7.85 s
[OsBr(RN=CH=S)(CO)(PPh_3)$_2$] (VIII)	Ph	1902		0.62 t		2.5	
[OsH(RN=CH=S)(CO)(PPh_3)$_2$][d] (IX)	Ph	1904	2040	0.18 t		2.9	τ(OsH) 23.4, $^2J(PH)_{cis}$ = 17 Hz
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XII)	Me			−0.26 d of d	10.0/4.0		τ(Me) 7.49 d, ^4J(PH) = 4 Hz
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XII)	Et			−0.36 d of d	11.2/4.5		
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XIV)	Et			0.48 t		1.8	
[$IrCl_2$(RN=CH=S)(PPh_3)$_2$] (XIV)	Ph			−0.26 t		2.5	
[$IrBr_2$(RN=CH=S)(PPh_3)$_2$] (XIV)	Ph			−0.29 t		2.5	

[a] NMR spectra run in $CDCl_3$ solution. Key: s = singlet, d = doublet, t = triplet, q = quartet. [b] Benzene solvate $\tau(C_6H_6)$ 2.76. [c] Chloroform solvate $\tau(CHCl_3)$ 2.76. [d] Acetone solvate $\tau(Me_2CO)$ 7.9.

N,S-donor character of the thioformamide ligands have been established by infrared and NMR spectroscopy. A preliminary report on this work has previously been published.[11]

Experimental Section

Hydrido complexes were prepared as previously described,[12] isothiocyanates were used as purchased from the Maybridge Chemical Co. Ltd., and reagent grade organic solvents were degassed prior to use. All reactions were performed under a nitrogen atmosphere but the products were worked up in air. Unless otherwise indicated, products were purified by washing successively with methanol and light petroleum (bp 60–80 °C) and then recrystallizing from dichloromethane–methanol and 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, University College London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. The rather poor analysis data obtained in several instances reflect the strong tendency of these complexes to occlude small amounts of solvent. Proton and phosphorus-31 NMR spectra were obtained at 90 and 36.43 MHz, respectively, using a Bruker HFX 90 NMR spectrometer with Fourier transform facility. Infrared spectra were run as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Spectroscopic data are recorded in Tables II (infrared and ^{1}H NMR) and III (^{31}P NMR).

Carbonylchloro(*N*-phenylthioformamido)bis(triphenylphosphine)ruthenium(II)—Stereochemistry VIII. A mixture of phenyl isothiocyanate (0.2 mL) and chlorocarbonylhydridotris(triphenylphosphine)ruthenium (0.34 g) in benzene (20 mL) was heated under reflux for 5 min. The resultant yellow solution was cooled to ambient temperature, filtered, concentrated under reduced pressure, and then diluted with methanol (10 mL) to precipitate a yellow crystalline solid. The precipitate was filtered off and then purified and recrystallized as described above to yield bright yellow crystals (0.17 g, 61%).

The following were similarly prepared using the appropriate ligand: carbonylchloro(*N*-*p*-tolylthioformamido)bis(triphenylphosphine)-

Table III. ^{31}P NMR Data[a]

Complex and stereochemistry	R	δ, ppm	$^2J(PP')$, Hz
$[RuCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VIII)	Ph	35.85 s	
$[RuCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$[b] (VIII)	*p*-tol	36.52 s	
$[RuCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VIII)	Et	36.12 s	
$[Ru(OCOCF_3)(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VIII)	Ph	38.27 s	
$[Ru(RN{=}CH{-}S)_2(PPh_3)_2]$	Ph	50.79 s	
$[Ru(RN{=}CH{-}S)_2(PPh_3)_2]$	Me	50.73 s	
$[OsCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VI)	Ph	5.73, −1.31 AB pattern	12.0
$[OsCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VI)	*p*-tol	5.76, −1.17 AB pattern	11.0
$[OsBr(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VI)	Ph	5.89, −3.38 AB pattern	11.0
$[OsCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VI)	Me	−4.72, −6.03 AB pattern	8.5
$[OsCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$[b] (VI)	Et	−5.57, −7.18 AB pattern	7.0
$[Os(OCOCF_3)(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VI)	Ph	2.65, 0.30 AB pattern	12.0
$[OsCl(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (VIII)	Ph	7.84 s	
$[IrCl_2(RN{=}CH{-}S)(PPh_3)_2]$[b] (XII)	Me	−28.31, −35.62 AB pattern	12.0

[a] Spectra taken in $CDCl_3$ unless otherwise indicated and referenced to external H_3PO_4 in the sense that positive values are to low field. All spectra proton decoupled. [b] Spectra taken in CD_2Cl_2; other conditions as above.

ruthenium(II)—stereochemistry VIII as yellow crystals (77%) and carbonylchloro(*N*-ethylthioformamido)bis(triphenylphosphine)ruthenium(II)—stereochemistry VIII as yellow crystals (80%), the reflux time in the latter case was 15 min.

Bromocarbonyl(*N*-phenylthioformamido)bis(triphenylphosphine)ruthenium(II)—stereochemistry VIII was similarly prepared from phenyl isothiocyanate and bromocarbonylhydridotris(triphenylphosphine)ruthenium and was purified and crystallized as described above to yield bright yellow crystals (86%).

Carbonyltrifluoroacetato(*N*-phenylthioformamido)bis(triphenylphosphine)ruthenium(II)—Stereochemistry VIII. A solution of phenyl isothiocyanate (0.2 g) and carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.3 g) in benzene (20 mL) was heated under reflux for 20 min and then cooled to ambient temperature, filtered, and 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 a yellow solid. The precipitate was filtered off and then purified and recrystallized as described above to yield yellow crystals (0.23 g, 76%).

Carbonylhydrido(*N*-phenylthioformamido)bis(triphenylphosphine)ruthenium(II). Carbonyldihydridotris(triphenylphosphine)-ruthenium (0.6 g) and phenyl isothiocyanate (0.2 mL) were heated under reflux in benzene (20 mL) for 80 min. The clear yellow solution was cooled to ambient temperature, filtered and concentrated under reduced pressure, and then diluted with methanol (10 ml) to precipitate a yellow solid. The precipitate was washed successively with methanol and light petroleum and then triturated with acetone and filtered. The filtrate containing an intractable product (see Discussion section) was discarded and the pale yellow solid was washed with acetone and light petroleum to give the required product as pale yellow microcrystals (0.24 g, 45%).

Bis(*N*-phenylthioformamido)bis(triphenylphosphine)ruthenium(II)–Benzene (4/1). A mixture of phenyl isothiocyanate (0.2 mL) and dihydridotetrakis(triphenylphosphine)ruthenium (0.4 g) was heated under reflux in benzene (20 mL) for 3 h. The resultant yellow-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 then diluted with methanol (10 mL) to precipitate a yellow solid. The precipitate was filtered off and then purified and crystallized as described above to yield yellow microcrystals (0.27 g, 69%).

Bis(*N*-methylthioformamido)bis(triphenylphosphine)ruthenium(II) was similarly prepared using methyl isothiocyanate and was purified and crystallized as described above to yield yellow microcrystals (0.22 g, 56%).

Carbonylchloro(*N*-phenylthioformamido)bis(triphenylphosphine)osmium(II)—Stereochemistry VI. A mixture of phenyl isothiocyanate (0.2 mL) and carbonylchlorohydridotris(triphenylphosphine)osmium (0.3 g) in benzene (20 mL) was heated under reflux for ca. 3 h. The pale yellow solution was cooled to ambient temperature, filtered and concentrated under reduced pressure, and then diluted with methanol (10 mL) to precipitate a very pale yellow solid. The precipitate was filtered off and then purified and crystallized as described above to yield pale yellow microcrystals (0.21 g, 70%).

Carbonylchloro(*N*-*p*-tolylthioformamido)bis(triphenylphosphine)osmium(II)—stereochemistry VI was similarly prepared using *p*-tolyl isothiocyanate and heating the reaction mixture for 90 min. The product was purified and crystallized as described above to yield pale yellow microcrystals (71%).

Bromocarbonyl(*N*-phenylthioformamido)bis(triphenylphosphine)osmium(II)—stereochemistry VI was similarly prepared by heating a mixture of phenyl isothiocyanate (0.2 mL) and bromocarbonylhydridotris(triphenylphosphine)osmium (0.36 g) under reflux in benzene (20 mL) for 2 h. Purification and recrystallization of the product as described above gave yellow microcrystals (0.22 g, 69%).

Carbonylchloro(*N*-methylthioformamido)bis(triphenylphosphine)osmium(II)—stereochemistry VI was similarly prepared by heating a mixture of methyl isothiocyanate (0.1 g) and carbonylchlorohydridotris(triphenylphosphine)osmium (0.5 g) under reflux in benzene (20 mL) for 90 min. The product was purified and crystallized as described above to yield pale yellow microcrystals (0.18 g, 63%).

Carbonylchloro(*N*-ethylthioformamido)bis(triphenylphosphine)-osmium(II)—stereochemistry VI was similarly prepared using ethyl isothiocyanate (0.2 mL) and heating the mixture under reflux for 5 min. The product was purified and crystallized as described above to yield pale yellow microcrystals (0.21 g, 70%).

Carbonyl(*N*-phenylthioformamido)(trifluoroacetato)bis(triphenylphosphine)osmium(II)–Chloroform (2/1)—Stereochemistry VI. A mixture of phenyl isothiocyanate (0.2 mL) and carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)osmium (0.4 g) in benzene (20 mL) was heated under reflux for 2.5 h. The bright 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 chloroform and then diluted with light petroleum (10 mL) to precipitate the required product as a yellow solid. The precipitate was filtered off, washed thoroughly with light petroleum, and crystallized from chloroform/light petroleum as yellow microcrystals (0.19 g, 57%).

Carbonylchloro(*N*-phenylthioformamido)bis(triphenylphosphine)osmium(II)—Stereochemistry VIII. A mixture of phenyl isothiocyanate (0.2 mL) and carbonylchlorohydridotris(triphenylphosphine)osmium (0.3 g) in toluene (20 mL) was heated under reflux for 3 h. The resultant yellow 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. The precipitate was filtered off and then purified and crystallized as described above to yield yellow crystals (0.2 g, 66%).

The following were similarly prepared using the appropriate isothiocyanate and osmium precursor: carbonylchloro(*N*-*p*-tolylthioformamido)bis(triphenylphosphine)osmium(II)—stereochemistry VIII as yellow crystals (83%) and carbonylbromo(*N*-phenylthioformamido)bis(triphenylphosphine)osmium(II)—stereochemistry VIII as yellow crystals (83%).

Carbonylhydrido(*N*-phenylthioformamido)bis(triphenylphosphine)osmium(II)–Acetone (4/3). A mixture of phenyl isothiocyanate (0.2 mL) and carbonyldihydridotris(triphenylphosphine)osmium (0.5 g) in toluene (20 mL) was heated under reflux for 8 h. The yellow solution was cooled to ambient temperature and filtered and then concentrated to small volume under reduced pressure and diluted with methanol (10 mL) to precipitate a yellow solid. The precipitate was filtered off, washed successively with methanol and light petroleum and then triturated with acetone and filtered. The filtrate containing an intractable product (see Discussion section) was discarded; the pale yellow solid was washed with acetone and light petroleum to give pale yellow microcrystals (0.12 g, 41%).

Dichloro(*N*-methylthioformamido)bis(triphenylphosphine)iridium(III)—Stereochemistry XII. A mixture of methyl isothiocyanate (0.1 g) and *trans*-dichlorohydridotris(triphenylphosphine)iridium (0.35 g) in benzene (20 mL) was heated under reflux for ca. 1 h. The resultant yellow 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. The precipitate was filtered off and then purified and crystallized as described above to yield yellow microcrystals (0.16 g, 57%).

Dichloro(*N*-ethylthioformamido)bis(triphenylphosphine)iridium(III)—Stereochemistry XII. Ethyl isothiocyanate (0.2 mL) was added to *trans*-dichlorohydridotris(triphenylphosphine)iridium (0.4 g) in benzene (20 mL), and the mixture was heated under reflux for ca. 15 min. The yellow solution was cooled to ambient temperature, filtered, concentrated to small volume under reduced pressure, and then diluted with ethanol (10 mL) to precipitate the product as a yellow solid. The precipitate was purified and crystallized as described above to yield pale yellow microcrystals (0.18 g, 62%).

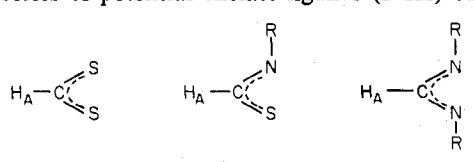
Dichloro(*N*-ethylthioformamido)bis(triphenylphosphine)iridium(III)—stereochemistry XIV was similarly prepared by heating a mixture of ethyl isothiocyanate (0.2 mL) and *trans*-dichlorohydridotris(triphenylphosphine)iridium (0.4 g) under reflux in benzene (20 mL) for ca. 1 h. Recrystallization from dichloromethane–ethanol gave the required product as yellow microcrystals (0.19 g, 65%) contaminated with traces of isomer XII.

Dichloro(*N*-phenylthioformamido)bis(triphenylphosphine)iridium(III)—Stereochemistry XIV. A mixture of phenyl isothiocyanate (0.2 mL) and *trans*-dichlorohydridotris(triphenylphosphine)iridium (0.35 g) in benzene (20 mL) was heated under reflux for 1 h. The resultant yellow solution was cooled and filtered and then concentrated under reduced pressure and diluted with methanol (10 mL) to precipitate the required product as a yellow solid. The precipitate was filtered off and then purified and crystallized as described above to yield yellow crystals (0.22 g, 71%).

Dibromo(*N*-phenylthioformamido)bis(triphenylphosphine)iridium(III)—stereochemistry XIV was similarly prepared by heating a mixture of *trans*-dibromohydridotris(triphenylphosphine)iridium (0.4 g) and phenyl isothiocyanate (0.2 mL) under reflux in benzene (20 mL) for 3 h and was purified and crystallized as described above to yield yellow crystals (0.18 g, 55%).

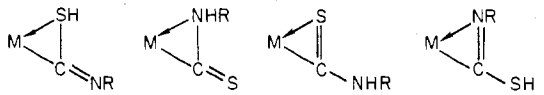
Results and Discussion

The *N*-alkyl- and *N*-arylthioformamide anions ($RN{=}\overline{C}H{=}S$) discussed in this paper are members of a related series of potential chelate ligands (I–III) currently



I II III

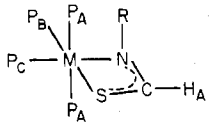
under investigation in our laboratory.[1,13] All three ligand types (I–III) have in common a characteristic low-field proton NMR resonance [τ(CH) ca. −4.0 to +2.5] arising from the central proton of the chelate ligand. Moreover, the resonance positions for the thioformamide ligands [II, τ(CH) −0.51 to +1.92] are approximately midway between those of the dithioformate [I, τ(CH) −4.0 to +0.5][1] and formamidinate [III, τ(CH) +0.68 to +2.26][13] ligands. Therefore, since structures I and III have been established by diffraction methods for the coordinated dithioformate[14,15] and *N*,*N*′-di-*p*-tolylformamidinate[13] ligands, respectively, it seems highly probable that the coordinated thioformamide ligands adopt the chelate structure II. Confirmation of this conclusion is provided by infrared spectroscopic data. The spectra of the thioformamido complexes show bands at ca. 1570–1500, 1290–1200, and 930–890 (w) cm^{-1} attributable to the formamide ligands and very similar to those observed for the closely related thiobenzamide [$RN{=}C(CH_2Ph){=}S$][10] and thioacetamide [$RN{=}C(Me){=}S$][9a] ligands. The N,S-chelate character of the latter ligand in the complex $\{NbCl_3[MeN{=}C(Me){=}S]_2\}$ has been established by x-ray diffraction methods.[9b] Finally, the absence of bands attributable to ν(NH) or ν(SH) at ca. 3500–3300 and ca. 2650–2550 cm^{-1}, respectively, leads us to conclude that the alternative ligand structures (IVa–d) are



IVa IVb IVc IVd

highly improbable in the present complexes.

Spectroscopic data also provide valuable evidence concerning the stereochemistry of the new thioformamido complexes. The low-field (τ(CH)) resonances of all three chelate ligands (I–III) show coupling [^4J(PH)] of the central hydrogen to the phosphorus atoms of adjacent phosphine ligands. Values of the coupling constants for the thioformamide complexes [V,

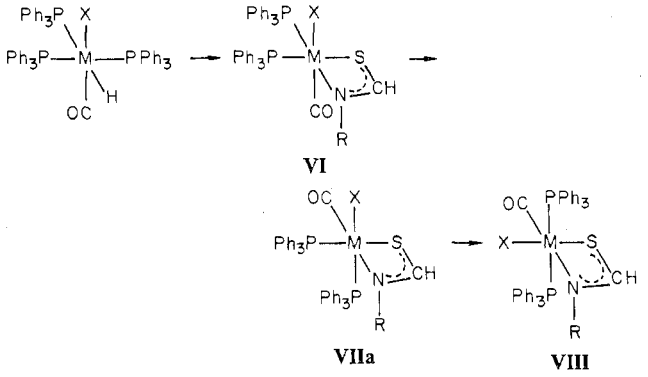


V

$^4J(P_AH_A) \simeq 2.5$ Hz, $^4J(P_BH_A) \simeq 8$–10 Hz, and $^4J(P_CH_A) \simeq 1.5$–4 Hz] are in good agreement with comparable data recorded for chelate dithioformato[1] and *N*,*N*′-*p*-tolylformamidinato[13] derivatives. The methyl protons in the *N*-methylformamido complexes couple with the central proton of the formamide ligand [^4J(HH) = ca. 1.0 Hz] and with the phosphorus nucleus of a trans phosphine ligand [^4J(PH) = ca. 1–4 Hz].

The hydrides $[MHX(CO)(PPh_3)_3]$ (M = Ru or Os; X = Cl, Br, or $OCOCF_3$) react with alkyl or aryl isothiocyanates (RNCS) in boiling benzene or toluene to yield products of stoichiometry $[MX(RN{=}CH{=}S)(CO)(PPh_3)_2]$ each of which is apparently capable of existing in three isomeric forms (Scheme I). For several of the osmium complexes all three isomers were detected spectroscopically but usually only one or two isomers could be isolated in a pure form. For the more labile ruthenium complexes only thermodynamically preferred isomers of stereochemistry VIII were detected and isolated; the conditions necessary to induce reaction between the precursors $[RuHX(CO)(PPh_3)_3]$ and the isothiocyanates (RNCS) are apparently more than sufficient to drive the isomerization process through to yield the thermodynamically preferred product. However, with the corresponding osmium precursors $[OsHX(CO)(PPh_3)_3]$ products of stereochemistry VI were isolated under mild conditions (boiling benzene) and isomerized to species of stereochemistry VIII on more vigorous treatment (boiling toluene). Finally, using alkyl isothiocyanates (RNCS, R = Me or Et) and mild reaction conditions for a more prolonged reaction time (boiling benzene, ca. 3 h) the intermediate osmium products of stereochemistry VIIa

Scheme I



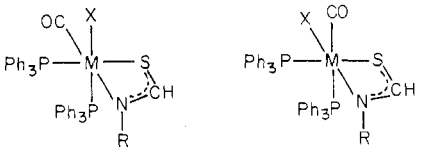
were detected in isomer mixtures but were not isolated.

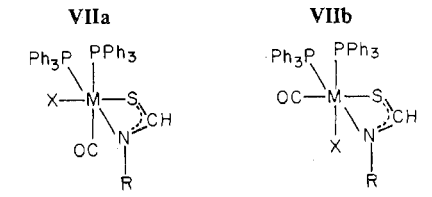
The complexes $[OsX(RN{=}CH{-}S)(CO)(PPh_3)_2]$ prepared under mild conditions each display a low-field proton NMR spectrum comprising a doublet of doublets [$^4J(PH)_{trans}$ = ca. 8–9 and 1.5–4 Hz] and a ^{31}P NMR spectrum consisting of an AB pattern. Infrared data for these complexes [ν(CO) ca. 1920–1938 cm^{-1}] are consistent with carbonyl trans to chloride.[17] Therefore, given the stereochemistry of the precursors $[OsHX(CO)(PPh_3)_3]$, it seems probable that these complexes, the initial products in Scheme I, have the proposed stereochemistry VI analogous to that found for the corresponding dithioformato complexes prepared under similar conditions.[1]

Stereochemistry VI is also supported by the NMR data obtained for these complexes. The relatively large coupling [$^4J(PH)$ = ca. 8–9 Hz] observed in the low-field (thioformamide CH) resonance pattern of each complex is indicative of a phosphine ligand trans to the sulfur atom of the thioformamide ligand.[1] Moreover, the appearance of a coupling $^4J(PH)$ between the methyl group of the *N*-methylthioformamide ligand and a phosphorus nucleus (confirmed by ^{31}P broad band decoupling) strongly implies that the second phosphine ligand is situated trans to the nitrogen donor atom of the formamide ligand.

The products $[MX(RN{=}CH{-}S)(CO)(PPh_3)_2]$ obtained when M = Ru and R = aryl or, by using more prolonged and/or vigorous reaction conditions, when M = Os and R = aryl have spectroscopic properties indicative of stereochemistry VIII. In particular the low-field proton NMR pattern comprises a triplet [$^4J(PH)_{cis}$ = 2.5 Hz] and the ^{31}P NMR pattern (proton decoupled) consists of a singlet. The infrared data [ν(CO) ca. 1900–1930 cm^{-1}] are consistent with the presence of carbonyl trans to nitrogen rather than sulfur[18] and thus fully establish stereochemistry VIII.

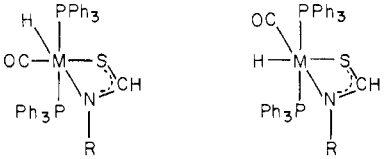
Finally, the intermediate isomers $[MX(RN{=}CH{-}S)(CO)(PPh_3)_2]$ (M = Os; R = Me or Et) observed in solution but not isolated have spectroscopic properties [low-field proton NMR doublet of doublets $^4J(PH)$ = ca. 9.0 and <2 Hz; ^{31}P NMR, AB pattern] broadly compatible with four possible stereochemical arrangements (VIIa–d)[20] but finally attributed to stereochemistry VIIa on the basis of the detailed arguments given below. The presence of a large (ca. 8–10 Hz) coupling [$^4J(PH)_{trans}$] similar to that found in the spectra of the corresponding dithioformato complexes[1] but absent from those of the *N,N'*-di-*p*-tolylformamidinato derivatives[13] strongly implies that the equatorial phosphine ligand is trans to the sulfur rather than the nitrogen donor atom of the thioformamide ligand, and therefore favors VIIa or VIIb rather than VIIc or VIId. If, as we surmise, the final isomer (Scheme I) has stereochemistry VIII with carbonyl trans to nitrogen and the anionic ligand X trans to sulfur, then stereochemistry VIIa is more probable than VIIb for the intermediate in the transformation VI → VIII. Thus transposition of PPh_3 with

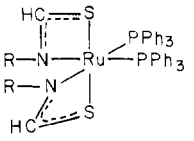




CO and PPh_3 with X converts VI to VIIa and VIIa to VIII, respectively (Scheme I).

The dihydrides $[MH_2(CO)(PPh_3)_3]$ (M = Ru or Os) react with phenyl isothiocyanate in boiling benzene (M = Ru) or toluene (M = Os) to afford products of stoichiometry $[MH(PhN{=}CH{-}S)(CO)(PPh_3)_2]$. The second hydride ligand in the complexes $[MH_2(CO)(PPh_3)_2]$ is reluctant to participate in the reaction and its partial removal under prolonged and/or vigorous reaction conditions leads to the formation of a mixture of products. These include, in addition to the species $[MH(PhN{=}CH{-}S)(CO)(PPh_3)_2]$, the complex $[Ru(PhN{=}CH{-}S)_2(CO)(PPh_3)]$, which was tentatively identified by its low-field ^1H NMR spectrum [τ(CH) 0.56 d, $^4J(PH)$ = 6 Hz; τ(CH) 1.09, d, $^4J(PH)$ < 2 Hz] but not isolated, and new sulfur-containing products of unknown constitution. The latter species, which are the subject of a separate investigation, also contaminate the complexes $[MH(PhN{=}CH{-}S)(CO)(PPh_3)_2]$ and are removed by extracting with acetone. The new products $[MH(PhN{=}CH{-}S)(CO)(PPh_3)_2]$ are assigned stereochemistry IX on the



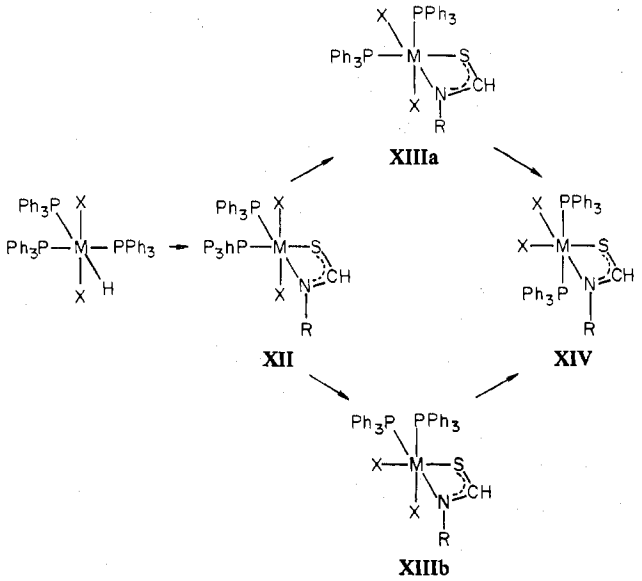


XI

basis of their proton NMR data (Table II) which establish the presence of hydride and thioformamide ligands both cis to a pair of mutually equivalent phosphine ligands. The τ(MH) values are characteristic of hydride trans to nitrogen rather than sulfur and thus support stereochemistry IX rather than the only possible alternative X. The absence of a detectable coupling $^4J(HH')$ between the hydride ligand and the central proton of the RN=CH–S ligand confirms this assignment.

Isothiocyanates react readily with *both* hydride ligands in $[RuH_2(PPh_3)_4]$ to yield bis(thioformamido) complexes $[Ru(RN{=}CH{-}S)_2(PPh_3)_2]$. For each of the products the low-field proton NMR pattern comprises a doublet [$^4J(PH)$ = ca. 2.5–3.0 Hz] and the proton-decoupled ^{31}P spectrum consists of a singlet. The low-field doublet pattern indicates that the phosphine ligands are inequivalent *with respect to a given thioformamide group* and therefore eliminates trans phosphine structures for which a low-field triplet [$^4J(PH)_{cis}$ > 0 Hz] or singlet [$^4J(PH)_{cis}$ = 0 Hz] pattern would be expected. The ^{31}P NMR singlet establishes that the phosphines

Scheme II[a]



[a] M = Ir.

are equivalent with respect to the complex as a whole, and the small size of the coupling [$^4J(PH)_{trans}$] in the low-field proton NMR doublet indicates that the phosphines are probably not trans to the sulfur atoms of the thioformamide ligands. Stereochemistry XI is the only one consistent with all the above observations. Strong supporting evidence for this assignment is provided by an x-ray diffraction study which reveals an analogous stereochemistry for the closely related pyridine-2-thiolato complex $[Ru(NC_5H_4S)_2(PPh_3)_2]$.[21]

The products of stoichiometry $[IrCl_2(RN{=}CH{-}S)(PPh_3)_2]$ obtained by treating the iridium hydrides $[IrHX_2(PPh_3)_3]$ (trans X; X = Cl or Br) with alkyl or aryl isothiocyanates are apparently capable of existing in at least two isomeric forms. If the isomerization reaction follows a course parallel to that proposed for the ruthenium and osmium complexes $[MX(RN{=}CH{-}S)(CO)(PPh_3)_2]$, then the possible isomeric forms are XII, XIIIa or XIIIb and XIV (Scheme II). The low-field proton NMR patterns of the *N*-arylthioformamide products each comprise a triplet [τ(CH) ca. −0.25 t, $^4J(PH)$ = ca. 2.5 Hz] indicative of stereochemistry XIV. However, the low-field patterns of the corresponding *N*-alkylthioformamido complexes each comprise a doublet of doublets consistent with three possible stereochemical arrangements (XII, XIIIa, or XIIIb). The occurrence of a relatively large coupling [$^4J(PH)$ = ca. 10 Hz] similar to those observed in the corresponding dithioformato complexes but not in their *N,N'*-diarylformamidinato analogues that one phosphine ligand is situated trans to the sulfur atom of the (RN=CH-S) ligand. Moreover the presence of a substantial coupling [$^4J(PH)$ = ca. 4 Hz] between the methyl group in the (MeN=CH-S) derivative and a phosphorus nucleus (confirmed by ^{31}P decoupling) strongly suggests that the second phosphine ligand is trans to the nitrogen atom of the (MeN=CH-S) ligand. These observations establish XII rather than XIIIa or XIIIb as the preferred stereochemistry for the alkyl products. Attempts to synthesize *N*-alkylthioformamido iridium complexes of stereochemistry XIIIa or XIIIb either lead to the formation of materials too insoluble for meaningful NMR spectroscopy measurements or give products of stereochemistry XIV.

The tendency of these and related dithioformato[1] and formamidinato[13] complexes to undergo isomerization is dependent upon the nature of the chelate ligand concerned and decreases in the sequence (ArN=CH=NAr) > (ArN=CH=S) ≥ (AlkN=CH=S) > (S=CH=S). This trend presumably reflects the stronger coordinating power of sulfur relative to nitrogen in these complexes and implies that the isomerization reactions proceed via five-coordinate intermediates formed by semidissociation of the chelate ligand. A detailed study of the isomerization processes and the general reactivity displayed by complexes containing formamidinate, thioformamide, or dithioformate ligands is in progress and will be reported elsewhere.

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Registry No. VI(M = Os, X = Cl, R = Ph), 60252-44-0; VI(M = Os, X = Cl, R = *p*-tol), 63658-31-1; VI(M = Os, X = Br, R = Ph), 60173-35-5; VI(M = Os, X = Cl, R = Me), 60185-23-1; VI(M = Os, X = Cl, R = Et), 63658-32-2; VI(M = Os, X = $OCOCF_3$, R = Ph), 63678-15-9; VIII(M = Ru, X = Cl, R = Ph), 60185-24-2; VIII(M = Ru, X = Cl, R = *p*-tol), 63658-33-3; VIII(M = Ru, X = Cl, R = Et), 63658-34-4; VIII(M = Ru, X = Br, R = Ph), 60185-25-3; VIII(M = Ru, X = $OCOCF_3$, R = Ph), 63658-35-5; VIII(M = Os, X = Cl, R = Ph), 60185-22-0; VIII(M = Os, X = Cl, R = *p*-tol), 63701-17-7; VIII(M = Os, X = Br, R = Ph), 60208-78-8; IX(M = Ru, R = Ph), 63658-36-6; IX(M = Os, R = Ph), 63658-37-7; XI(R = Ph), 60173-39-9; XI(R = Me), 60173-40-2; XII(M = Ir, X = Cl, R = Me), 63658-38-8; XII(M = Ir, X = Cl, R = Et), 63658-39-9; XIV(M = Ir, X = Cl, R = Et), 63701-18-8; XIV(M = Ir, X = Cl, R = Ph), 63658-40-2; XIV(M = Ir, X = Br, R = Ph), 63658-41-3; $[RuHCl(CO)(PPh_3)_3]$, 16971-33-8; $[RuHBr(CO)(PPh_3)_3]$, 16971-34-9; $[RuH(OCOCF_3)(CO)(PPh_3)_2]$, 63701-15-5; $[RuH_2(CO)(PPh_3)_3]$, 25360-32-1; $[RuH_2(PPh_3)_4]$, 19529-00-1; $[OsHCl(CO)(PPh_3)_3]$, 16971-31-6; $[OsHBr(CO)(PPh_3)_3]$, 16971-32-7; $[OsH(OCOCF_3)(CO)(PPh_3)_2]$, 63701-16-6; $[OsHz(CO)(PPh_3)_3]$, 12104-84-6; *trans*-$[IrHCl_2(PPh_3)_3]$, 28060-70-0; *trans*-$[IrHBr_2(PPh_3)_3]$, 63701-19-9; phenyl isothiocyanate, 103-72-0; *p*-tolyl isothiocyanate, 622-59-3; ethyl isothiocyanate, 542-85-8; methyl isothiocyanate, 556-64-9.

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