

Thiocarbamoyl Complexes of Ruthenium(II), Rhodium(III), and Iridium(III)

Anthony F. Hill,^{*,†} Derek A. Tocher,[‡] Andrew J. P. White,[§]
David J. Williams,[§] and James D. E. T. Wilton-Ely^{*,‡}

Research School of Chemistry, Institute of Advanced Studies, Australian National University,
Canberra, Australian Capital Territory, Australia, Department of Chemistry, University
College London, London WC1H 0AJ, U.K., and Department of Chemistry, Imperial College
London, London SW7 2AZ, U.K.

Received June 22, 2005

The reaction of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**1**) or $[\text{Ru}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2]$ with *N,N*-dimethylthiocarbamoyl chloride provides $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\text{CO})_2(\text{PPh}_2)_2]\text{Cl}$ (**2·Cl**), thermolysis of which yields $[\text{Ru}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_2)_2]$ (**3**). Treatment of **2·Cl** with NaBH_4 leads to carbonyl substitution and formation of $[\text{RuH}(\eta^2\text{-SCNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ (**4**), which is readily converted to an alternative isomer of $[\text{RuCl}(\eta^2\text{-SCNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ (**5**, Cl *trans* to S) on treatment with hydrochloric acid. The reaction of **2·PF₆** with $\text{Na}[\text{S}_2\text{CNMe}_2]$ gives $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)]$ (**6**), which is also the product of the reaction of **1** with $\{\text{Me}_2\text{NC}(\text{S})\}_2\text{S}$. $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ (**7·Cl**) is isolated from the reaction between $[\text{Ru}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})(\text{PPh}_3)_3]$ and $\text{Me}_2\text{NC}(\text{S})\text{Cl}$. $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$, $[\text{RhCl}(\text{PPh}_3)_3]$, or $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$ (cod = cycloocta-1,5-diene) react with *N,N*-dimethylthiocarbamoyl chloride to provide $[\text{Rh}(\eta^2\text{-SCNMe}_2)\text{Cl}_2(\text{PPh}_3)_2]$ (**8**), while $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ provides the metallacyclic complex $[\text{Rh}\{\kappa^2\text{-C}(\text{NMe}_2)\text{SC}(\text{=S})\}\text{Cl}_2(\text{PPh}_3)_2]$ (**9**). The complexes $[\text{IrCl}(\text{CA})(\text{PPh}_3)_2]$ react with $\text{Me}_2\text{NC}(\text{=S})\text{Cl}$ to give the salts $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CA})(\text{PPh}_3)_2]\text{Cl}$ (A = O **10·Cl**, S **12·Cl**). Photolysis of **10·Cl** or treatment with dimethylamine provides the neutral complex $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}_2(\text{PPh}_3)_2]$ (**11**), which may be obtained directly by reaction of $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ with $\text{Me}_2\text{NC}(\text{S})\text{Cl}$. Treatment of **10·Cl** with NaBH_4 or NaOEt proceeds via attack at the CO ligand to form $[\text{Ir}(\eta^2\text{-SCNMe}_2)\{\eta^1\text{-C}(\text{=O})\text{H}\}]\text{Cl}(\text{PPh}_3)_2]$ (**13**) or $[\text{Ir}(\eta^2\text{-SCNMe}_2)\{\eta^1\text{-C}(\text{=O})\text{OEt}\}]\text{Cl}(\text{PPh}_3)_2]$ (**14**), respectively.

Introduction

We have recently been concerned with the organometallic chemistry of what might be termed heteroacyls:¹ analogues of the familiar acyl ligand wherein the oxygen atom is replaced by a heavier chalcogen and/or the hydrocarbyl substituent is replaced by a heteroatom group (Scheme 1). The oldest members of this series are carbamoyl and thiocarbamoyl ligands, the former most commonly arising from the reactions of metal carbonyls with amines or amides.² For thiocarbamoyls, a range of synthetic strategies is available (Scheme 2) with varying degrees of general applicability. Mononuclear chalcocoacyls (i.e., $\text{L}_n\text{MC}(\text{=S})\text{R}$; R = hydrocarbyl) are the least widely studied, and by far the majority of these involve metals from groups 8 and 9,^{3–5} although we have obtained thioaroyl⁶ and very recently selenoaroyl^{1e} complexes of group 6 metals via single-atom sulfur or

selenium transfer agents in combination with alkylidyne complexes. Thioaroyls have been implicated in the formation of dithiocarboxylatoalkylidene⁷ and dithiocarboxylate complexes,^{6,8–11} and conversely a phosphino-stabilized example has arisen from the abstraction

(3) (a) Roper, W. R.; Town, K. G. *Chem. Commun.* **1977**, 781. (b) Collins, T. J.; Roper, W. R. *Chem. Commun.* **1976**, 1044. (c) Collins, T. J.; Roper, W. R. *Chem. Commun.* **1977**, 901. (d) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, 159, 73. (e) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1983**, 259, 215. (f) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, 157, 23. (g) Clark, G. R.; Collins, T. J.; Hall, D.; James, S. M.; Roper, W. R. *J. Organomet. Chem.* **1977**, 141, C5. (h) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *J. Organomet. Chem.* **2001**, 623, 109. (i) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *J. Organomet. Chem.* **2000**, 607, 27. (j) Elliott, G. P.; Roper, W. R. *J. Organomet. Chem.* **1983**, 250, C5. (k) Elliott, G. P.; Roper, W. R.; Waters, J. M. *Chem. Commun.* **1982**, 811. (l) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, 157, C23.

(4) Drews, R.; Edelmann, F.; Behrens, U. *J. Organomet. Chem.* **1986**, 315, 369.

(5) (a) Bedford, R. B.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 95. (b) Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, 17, 4249. (c) Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1998**, 3501. (d) Cannadine, J. C.; Hector, A.; Hill, A. F. *Organometallics* **1992**, 11, 2323.

(6) Cook, D. J.; Hill, A. F. *Chem. Commun.* **1997**, 955.

(7) Anderson, S.; Cook, D. J.; Hill, A. F.; Malget, J. M. *Organometallics* **2004**, 23, 2552.

(8) (a) Hill, A. F.; Malget, J. M. *J. Chem. Soc., Dalton Trans.* **1997**, 2003. (b) Anderson, S.; Hill, A. F.; Nasir, B. A. *Organometallics* **1995**, 14, 2987.

* To whom correspondence should be addressed. E-mail: a.hill@anu.edu.au; j.wilton-ely@ucl.ac.uk.

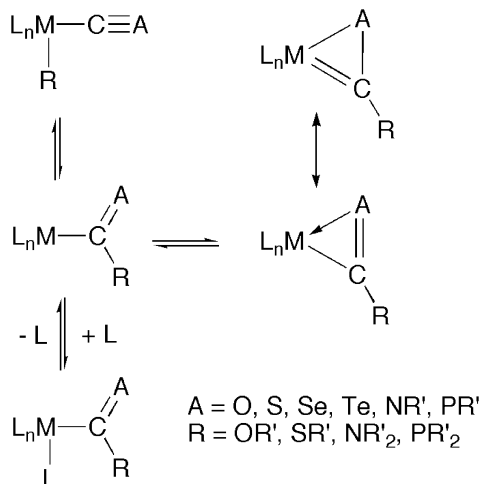
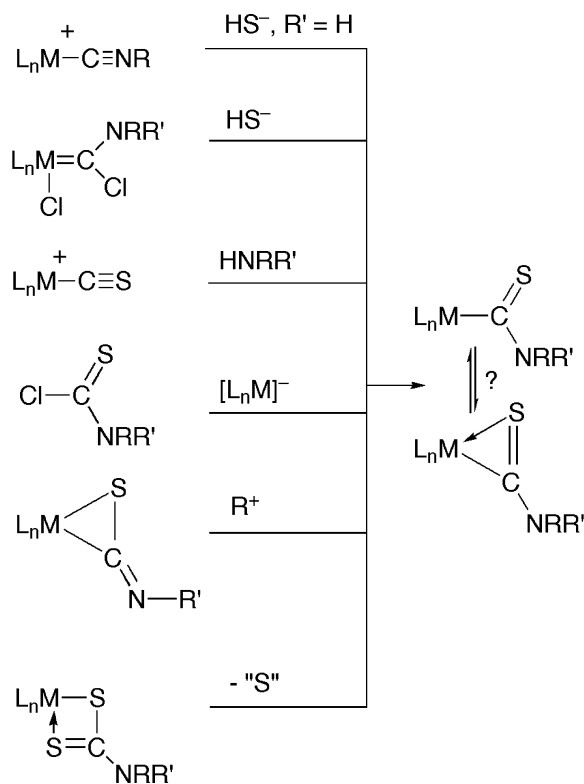
[†] Australian National University.

[‡] University College London.

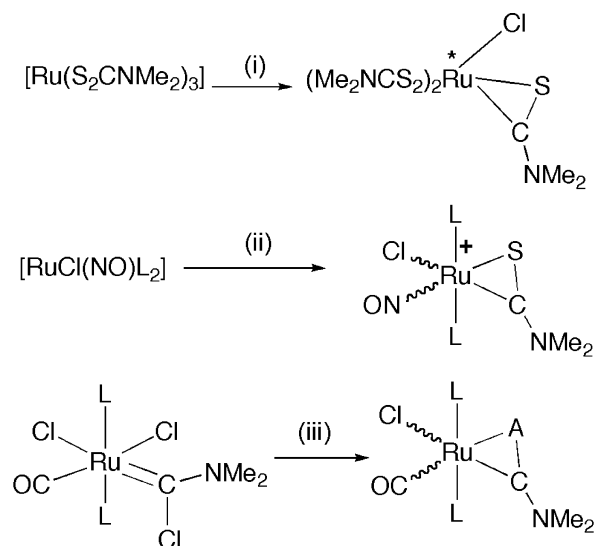
[§] Imperial College London.

(1) (a) Anderson, S.; Hill, A. F.; Ng, Y. T. *Organometallics* **2000**, 19, 15. (b) Anderson, S.; Cook, D. J.; Hill, A. F. *Organometallics* **2001**, 20, 2468. (c) Cook, D. J.; Hill, A. F. *Organometallics* **2003**, 22, 3502. (d) Anderson, A.; Berridge, T. E.; Hill, A. F.; Ng, Y. T.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, 23, 2686. (e) Caldwell, L. M.; Hill, A. F.; Willis, A. C. *Chem. Commun.* **2005**, 221.

(2) Angelici, R. J. *Acc. Chem. Res.* **1972**, 18, 335.

Scheme 1. Inter-relationship of Heteroacyl Coordination Modes

Scheme 2. Synthetic Approaches to Thiocarbamoyl Complexes


of sulfur from a dithiobenzoate by trimethylphosphine.¹² Bimetallic complexes with thioacyl,^{4,8b,13-16} selenoacyl,^{13,14} and recently telluroacyl¹⁷ ligands have been reported wherein the C-chalcogen unit transversely

Scheme 3^a


^a L = PPh₃. (i) hν, Ph₂C=O, CHCl₃; (ii) XC(S)NMe₂, X = Cl, PhN(C)S)NMe₂; (iii) NaAH, A = S, Se, Te.

bridges the metal-metal bond. The sporadic nature of research into chalcocyls has provided few situations where comparisons of structural and spectroscopic data are possible for a wide cohort of variations with all other factors held constant. The existence of a number of suitable species within groups 8 and 9 provides a basis for our investigations in this area. We have now addressed the synthesis of thiocarbamoyl (thiocarboxamido) complexes of ruthenium, iridium, and rhodium, some of which (or their isomers) were previously known but lacked structural and/or spectroscopic data.

Results and Discussion

Ruthenium Complexes. Previous approaches to the synthesis of thiocarbamoyl complexes of ruthenium (Scheme 3) have involved (i) photolytic sulfur abstraction from dithiocarbamate ligands;¹⁸ oxidative addition of Me₂NC(=S)Cl or PhN{C(=S)NMe₂}₂ to [RuCl(NO)(PPh₃)₂];¹⁹ or nucleophilic attack by hydrosulfide on a chloroaminocarbene complex [RuCl₂{=C(NMe₂)Cl}(CO)(PPh₃)₂].²⁰ This last approach offers the advantage that it could be extended to all the heavier chalcogens to provide the first complete series of complexes [Ru(η²-ACNMe₂)Cl(CO)(PPh₃)₂] (A = S, Se, Te) and mirrors the reactions of the chlorotoluidene complex [OsCl₂(=CClR)(CO)(PPh₃)₂] (R = C₆H₄Me-4), which similarly provided the first (and only) complete series of chalcocoyls [Os(η²-ACR)Cl(CO)(PPh₃)₂].²¹ Mononuclear carbamoyl complexes of ruthenium have a long if somewhat sparse

(9) Gill, D. S.; Green, M.; Marsden, K.; Moore, K.; Orpen, A. G.; Stone, F. G. A.; Williams, I. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 1343.

(10) Mercado, L. A.; Handwerker, B. M.; MacMillan, H. J.; Geoffroy, G. L.; Rheingold, A. L.; Owens-Waltermire, B. E. *Organometallics* **1993**, *12*, 1559.

(11) Kreissl, F. R.; Ullrich, N. *J. Organomet. Chem.* **1989**, *361*, C30.

(12) Kreissl, F. R.; Ullrich, N.; Wirsing, A.; Thewalt, U. *Organometallics* **1991**, *10*, 3275.

(13) (a) Byrne, P. G.; Garcia, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1215. (b) Ellis, D. D.; Farmer, J. M.; Malget, J. M.; Mullica, D. F.; Stone, F. G. A. *Organometallics* **1998**, *17*, 5540.

(14) Hill, A. F.; Nasir, B. A.; Stone, F. G. A. *Polyhedron* **1989**, *8*, 179.

(15) (a) Umland, H.; Behrens, U. *J. Organomet. Chem.* **1985**, *287*, 109. (b) Ziegler, W.; Umland, H.; Behrens, U. *J. Organomet. Chem.* **1988**, *344*, 235.

(16) (a) Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 1696. (b) Seyferth, D.; Womack, G. B.; Gallagher, M. K.; Cowie, M.; Hames, B. W.; Fackler, J. P. Jnr; Mazany, A. M. *Organometallics*, **1987**, *6*, 283.

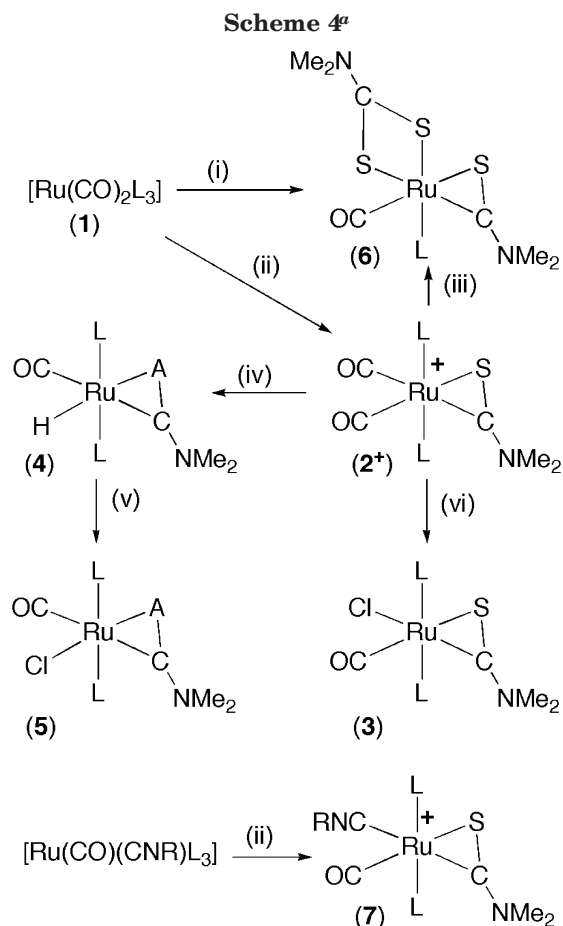
(17) Hulkes, A. J.; Hill, A. F.; Nasir, B. A.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 679.

(18) Miessler, G. L.; Pignolet, L. H. *Inorg. Chem.* **1979**, *18*, 210.

(19) Dean, W. K. *J. Organomet. Chem.* **1980**, *190*, 353.

(20) Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1982**, *233*, C59.

(21) (a) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570. (b) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167.

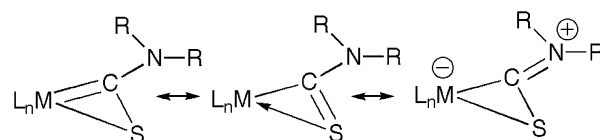


^a L = PPh₃, R = C₆H₃Me₂-2,6, (i) S(CSNMe₂)₂; (ii) ClC(S)NMe₂; (iii) Na[S₂CNMe₂]; (iv) NaBH₄; (v) HCl; (vi) EtOH, Δ.

history,^{22–27} which includes their implications in catalytic processes^{26,27} and the structural characterization of three examples.^{22a,26} The only mononuclear ruthenium thiocarbamoyl complex to have been structurally characterized, however, is the complex [Ru(η²-SCNMe₂)Cl(S₂CNMe₂)₂].¹⁸

The synthesis and reactivity of the new ruthenium thiocarbamoyl complexes to be described in this paper are summarized in Scheme 4. The reaction of [Ru(CO)₂(PPh₃)₃]²⁸ (1) with *N,N*-dimethylthiocarbamoyl chloride, Me₂NC(S)Cl, in dichloromethane or tetrahydrofuran leads at room temperature to the formation of the salt [Ru(η²-SCNMe₂)(CO)₂(PPh₃)₂]Cl (2·Cl), which may be isolated in yields of 90–95% by crystallization with ethanol or hexane. Despite the propensity of the exocyclic sulfur group of [Ru(η²-SCS)(CO)₂(PPh₃)₂]²⁹ for

Chart 1. Canonical Forms for *Dihapto* Thiocarbamoyl Coordination



reactions with electrophiles, the product of this complex with Me₂NC(S)Cl is also 2·Cl. It is not clear whether this involves a simple dissociation of the CS₂ ligand or if initial electrophilic attack is followed by extrusion of CS₂ from a metallacyclic dithiocarbamatothioacyl since no intermediates were detected. Given that the CS₂ ligand in the precursor is not considered labile under these conditions, we are inclined to suspect the latter process and note that one example of such a metallacycle has been identified previously, albeit in a bimetallic context.³⁰ The presence of the thiocarbamoyl group in 2⁺ is indicated by the appearance of absorptions at 1599 (ν_{CN}), 1219 and 916 (ν_{CS}) cm⁻¹ in the infrared spectrum (Nujol). From a comparison of these data with those for a range of thiocarbamoyl complexes of molybdenum¹ and the iridium complex [Ir(η²-SCNMe₂)Cl(CO)(PPh₃)₂]⁺ (1615, 995, 915 cm⁻¹, vide infra)¹⁹ it may be surmised that the thiocarbamoyl ligand adopts a *dihapto* mode of coordination, with a noncoordinated chloride counteranion. In contrast, the *monohapto* thiocarbamoyl complex [Fe{C(=S)NHMe}(CO)₂(η-C₅H₅)] is reported to give rise to a ν_{CS}-associated absorption at 1158 cm⁻¹.³¹ The ν_{CO} infrared absorptions at 2055 and 1995 cm⁻¹ for the related dithiomethoxycarbonyl complex [Ru(η²-SCSMe)(CO)₂(PPh₃)₂]⁺²⁹ also compare well with those at 2052 and 1989 cm⁻¹ (Nujol) for the complex 2⁺. The geometry at ruthenium involves *trans* phosphine ligands, as indicated by a singlet resonance (δ_P = 33.7) in the ³¹P{¹H} NMR spectrum. The ¹³C{¹H} NMR spectrum shows three low-field resonances attributable to the thiocarbonyl carbon (δ_C = 231.1, ²J_{CP} = 8.9 Hz) and the two chemically distinct carbonyl ligands (δ_C = 199.4, 199.9 ppm). In both the ¹H (2.42, 2.83 ppm) and ¹³C{¹H} (48.0, 49.1 ppm) NMR spectra, the resonances associated with the methyl groups indicate inequivalence, consistent with rotation around the N–C bond being arrested by the partial multiple character of this bond (Chart 1), a common observation in carbamoyl chemistry and a recurrent feature of the further complexes discussed below. The virtual triplet resonances due to the *ipso*, *ortho*, and *meta* carbon nuclei of the PPh₃ ligands confirm the *trans* geometry of the RuP₂ unit in complex 2a⁺. The FAB mass spectrum shows a molecular ion corresponding to [Ru(η²-SCNMe₂)(CO)₂(PPh₃)₂]⁺, with no peaks attributable to [RuCl(η²-CSNMe₂)(CO)(PPh₃)₂]. Spectroscopic data associated with the metal complex are not affected by metathesis of the counteranion, and the formulation was subsequently confirmed by X-ray crystallography of the hexafluorophosphate salt (2·PF₆) obtained as a chloroform monosolvate by diffusion of ethanol into a chloroform solution. The molecular structure of the cation 2⁺ is depicted in Figure 1 and approximates to a distorted

(22) (a) Wagner, H.; Jungbaur, A.; Thiele, G.; Behrens, H. Z. *Naturforsch.* **1979**, *34b*, 1487. (b) Behrens, H.; Jungbaur, A. Z. *Naturforsch.* **1979**, *34b*, 1477. (c) Jungbaur, A.; Behrens, H. Z. *Naturforsch.* **1979**, *34b*, 1641.

(23) Nonoyama, M. *Inorg. Chim. Acta* **1986**, *115*, 169.

(24) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 597.

(25) Ozawa, F.; Chikaoka, S.; Cao, X.; Yamamoto, A. *J. Organomet. Chem.* **1992**, *424*, 173.

(26) Gargulak, J. D.; Gladfelter, W. L. *Inorg. Chem.* **1994**, *33*, 253.

(27) Tsuji, Y.; Ohsumi, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1986**, *309*, 333.

(28) Cavit, B. E.; Grundy, K. R.; Roper, W. R. *Chem. Commun.* **1972**, 60.

(29) (a) Grundy, K. R.; Harris, R. O.; Roper, W. R. *J. Organomet. Chem.* **1975**, *90*, C34. (b) Clark, G. R.; Collins, T. J.; James, S. M.; Roper, W. R. *J. Organomet. Chem.* **1977**, *125*, C23. (c) Boniface, S. M.; Clark, G. R. *J. Organomet. Chem.* **1980**, *184*, 125.

(30) Burgmayer, S. J. N.; Templeton, J. L. *Inorg. Chem.* **1986**, *24*, 3939.

(31) Busetto, L.; Graziani, M.; Belluco, U. *Inorg. Chem.* **1971**, *10*, 78.

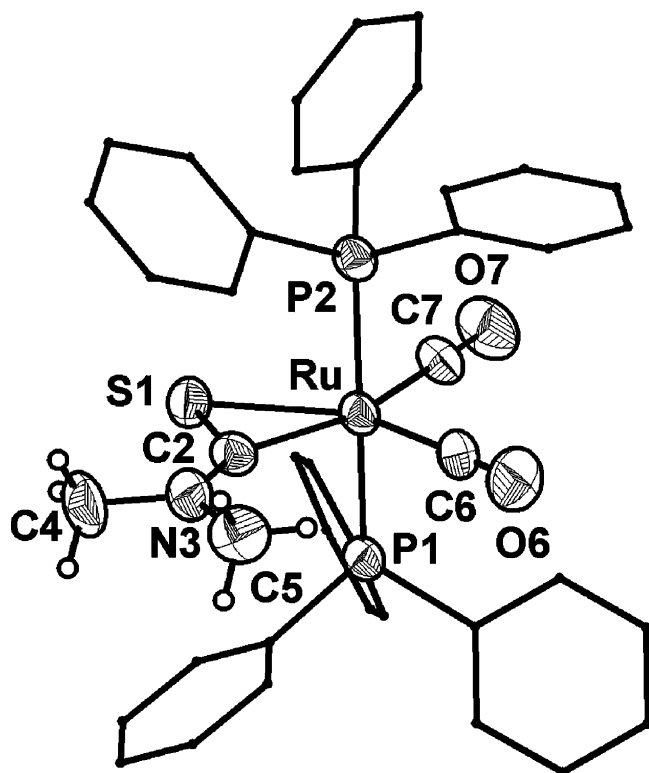


Figure 1. Molecular structure of the cation $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\text{CO})_2(\text{PPh}_3)_2]^+$ (2^+) in a crystal of $2 \cdot \text{PF}_6 \cdot \text{CHCl}_3$. (Phenyl groups simplified, 50% displacement ellipsoids.) Selected bond lengths (\AA) and angles (deg): Ru–C6 = 1.884(6), Ru–C7 = 1.919(6), Ru–C2 = 2.047(5), Ru–P1 = 2.4003(16), Ru–P2 = 2.4107(16), Ru–S1 = 2.4547(19), S1–C2 = 1.674(5), C2–N3 = 1.301(7), C6–Ru–C7 = 96.6(2), C6–Ru–C2 = 107.2(2), C6–Ru–P1 = 92.10(18), C7–Ru–P1 = 87.23(17), C2–Ru–P1 = 90.10(16), C6–Ru–P2 = 92.55(18), C7–Ru–P2 = 87.44(17), C2–Ru–P2 = 93.14(16), C7–Ru–S1 = 113.72(18), C2–Ru–S1 = 42.45(15), P1–Ru–S1 = 88.25(6), P2–Ru–S1 = 90.18(6), P1–Ru–P2 = 173.29(5), C7–Ru–C2 = 156.1(2), C6–Ru–S1 = 149.65(17), C2–S1–Ru = 55.63(19), S1–C2–Ru = 81.9(2), C2–N3–C5 = 122.9(5), C2–N3–C4 = 121.7(5), C5–N3–C4 = 115.4(5).

octahedral geometry with the mutually *trans* phosphine ligands displaying an angle of $173.29(5)^\circ$ between ruthenium–phosphorus vectors. The most informative structural features are associated with the equatorial plane containing carbonyl and thiocarbamoyl ligands. The ruthenium atom, the carbonyl ligands, and the heavy atoms of the thiocarbamoyl ligand are all approximately coplanar, consistent with electronic delocalization throughout the π -system involving these atoms. The C2–N3 distance of $1.301(7) \text{ \AA}$ is typical of a $\text{N}(\text{sp}^2)\text{-C}(\text{sp}^2)$ bond involving conjugation, and the Ru–C2 bond length of $2.047(5) \text{ \AA}$ suggests a degree of multiple bond character. The carbon atom of bidentate thioacyl ligands might be expected to show a modest degree of π -acidity, while the sulfur would be expected to have π -donor character. This appears to be reflected in the difference between the ruthenium carbonyl bond lengths, with that *trans* to the π -competitive thiocarbamoyl carbon [Ru–C7 $1.919(6) \text{ \AA}$] being somewhat longer than that *trans* to the π -basic sulfur donor [Ru–C6 $1.884(6) \text{ \AA}$]. These effects are presumably reduced as a result of the requisite distortion from octahedral geometry of C2, S1, C6, and C8 caused by the small bite

Table 1. IR Data for the Complexes $[\text{Ru}(\text{L})(\text{CO})_2(\text{PPh}_3)_2]^+$

L	$\nu_{\text{CO}}/\text{cm}^{-1}$	$k_{\text{CK}}/\text{N m}^{-1}$	ref
NO	2065, 2014	16.80	61
SCSMe	2055, 1995	16.56	29b
NNPh	1978, 2064	16.50	62
SCNMe ₂ (2^+)	2048, 1988	16.45	
CPh	2020, 1960	16.00	60

$$^a k_{\text{CK}} = 2.0191 \times 10^{-6} \text{ N m}^{-1} \times (\nu_1^2 + \nu_2^2).$$

angle of the thiocarbamoyl [C2–Ru–S1 $42.45(15)^\circ$]. The ruthenium carbonyl separations do however fall toward the short end of the range (consistent with their thermal inertness) despite the cationic charge on the complex, and this might be indicative of a net donor role for the bidentate thiocarbamoyl ligand. The bond lengths and angles of the thiirene unit are very similar to those for the related complex $[\text{Ru}(\eta^2\text{-SCSMe})(\text{CO})_2(\text{PPh}_3)_2]^+$ (see Table 1).⁷ The elongation of the Ru–C8 bond relative to Ru–C6 might suggest that it is this carbonyl ligand that is lost in subsequent reactions (e.g., with NaBH_4 to form 4).

On heating $2 \cdot \text{Cl}$ for 6 h in ethanol under reflux, decarbonylation occurs to give the neutral species $[\text{Ru}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (**3**) in good yield. This complex has been previously prepared by a different route.²⁰ A more facile decarbonylation process has been seen to ensue readily on reaction of $[\text{Ru}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2]$ with iodomethane to provide $[\text{Ru}(\eta^2\text{-SCSMe})\text{I}(\text{CO})(\text{PPh}_3)_2]$.²⁹ That the solvent plays a part in this process was clearly shown by the lack of any spectroscopic (IR) change upon heating the salt $2 \cdot \text{Cl}$ in refluxing tetrahydrofuran for 48 h. Pale yellow blocks of **3** suitable for an X-ray study were obtained by diffusion of a chloroform solution of the complex into ethanol, and the results of this study are summarized in Figure 2. As with 2^+ , the distorted octahedral geometry at ruthenium involves *trans* coordination of phosphine ligands with the remaining ligands lying in the equatorial plane. The complex displays *cis*-interligand angles in the range $88.44(10)^\circ$ to $109.71(8)^\circ$, the larger of these lying in the equatorial plane. The carbonyl–ruthenium separation is shorter [$1.828(10) \text{ \AA}$] than those for 2^+ , consistent with complex **3** being neutral. Again the thiocarbamoyl unit is planar, indicating sp^2 hybridization of the nitrogen atom and a short C2–N3 bond length reflecting multiple bond character. The dimensions of the thiocarbamoyl ligand are also included in Table S1 for comparison with those for 2^+ and other ruthena- and osmathiirenes.

The reaction of $2 \cdot \text{Cl}$ with an ethanolic solution of sodium borohydride leads to a clean reaction, in which the RuSC metallacycle is retained, that provides the neutral complex $[\text{RuH}(\eta^2\text{-SCNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ (**4**). The formulation of this colorless compound rests on spectroscopic observations. The presence of a hydride ligand is apparent as a triplet resonance ($\delta_{\text{H}} = -14.30$, $J_{\text{HP}} = 22.1 \text{ Hz}$) in the ^1H NMR spectrum due to coupling to two mutually *trans* phosphorus nuclei, a geometry also indicated by a singlet resonance ($\delta_{\text{P}} = 48.9$) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. While $^{13}\text{C}\{^1\text{H}\}$ NMR data ($\delta_{\text{C}} = 210.6$, $J_{\text{CP}} = 15.2 \text{ Hz}$) for the carbonyl ligand do not exclude the possibility of an alternative *trans*-dicarbonyl formulation *ttt*- $[\text{RuH}\{\eta^1\text{-C}(\text{=S})\text{NMe}_2\}(\text{CO})_2(\text{PPh}_3)_2]$, the observation that the $\nu(\text{CO})$ absorption at 1912 cm^{-1} in

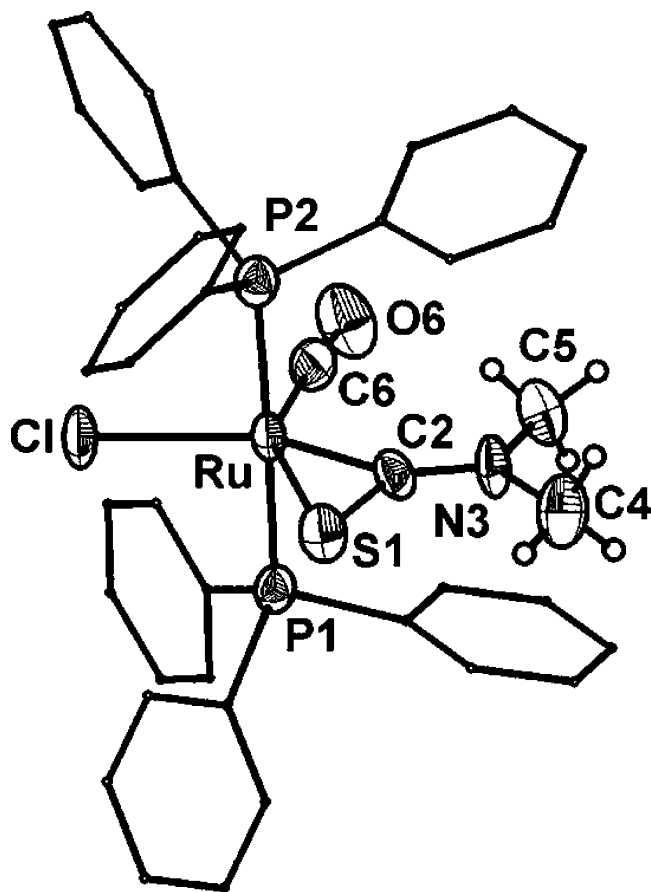


Figure 2. Molecular geometry of $[\text{Ru}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_3]$ (**3**) (Phenyl groups simplified, 50% displacement ellipsoids.) Selected bond lengths (\AA) and angles (deg): Ru–C6 = 1.828(10), Ru–C2 = 1.959(8), Ru–P2 = 2.374(3), Ru–P1 = 2.379(3), Ru–Cl = 2.468(2), Ru–S1 = 2.548(2), S1–C2 = 1.687(9), C2–N3 = 1.292(10), C6–Ru–C2 = 103.5(4), C6–Ru–P2 = 89.4(3), C2–Ru–P2 = 92.0(3), C6–Ru–P1 = 89.5(3), C2–Ru–P1 = 90.5(3), C6–Ru–Cl = 105.4(3), P2–Ru–Cl = 88.44(10), P1–Ru–Cl = 89.67(10), C2–Ru–S1 = 41.4(3), P2–Ru–S1 = 91.35(9), P1–Ru–S1 = 90.90(8), Cl–Ru–S1 = 109.71(8), P2–Ru–P1 = 177.44(9), C2–Ru–Cl = 151.1(3), C6–Ru–S1 = 144.9(3), C2–S1–Ru = 50.2(3), S1–C2–Ru = 88.3(4), C2–N3–C4 = 122.8(8), C2–N3–C5 = 121.0(8), C4–N3–C5 = 116.2(8).

the infrared spectrum is also the only $\nu(\text{CO})$ -associated absorption in the FT-Raman spectrum would appear to discount this possibility. The proposed formulation is also supported by the appearance of a molecular ion isotope cluster in the FAB mass spectrum, assigned to $[\text{RuH}(\eta^2\text{-CSNMe}_2)(\text{CO})(\text{PPh}_3)_2]^+$; none was observed corresponding to a dicarbonyl derivative. While loss of the thiocarbamoyl fragment is not a major feature of the FAB-MS of **2**, this fragment is readily lost from **4**, suggesting a facile reductive elimination of $\text{Me}_2\text{NC}(\text{S})\text{H}$. The replacement of one carbonyl ligand by a hydride, with *ultimate* retention of the bidentate thiocarbamoyl coordination, perhaps implicates the intermediacy of a formyl complex, e.g., $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\eta^1\text{-CHO})(\text{CO})(\text{PPh}_3)_2]$. This possibility is supported by the iridium chemistry described below. To further confirm the identity of **4**, its reaction with hydrochloric acid was investigated on the assumption that it would provide **3**. However, while the yellow product isolated, **5**, gave consistent ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and FAB-MS data, the infrared data included a carbonyl absorption at 1940

cm^{-1} , 20 cm^{-1} higher than for **3**, suggesting an alternative isomer with the carbonyl ligand *trans* to the thiocarbamoyl carbon. The crystal structure determination of **3** demonstrated the intuitive *trans* arrangement for the thiocarbamoyl sulfur (π -donor) and carbonyl (π -acid). The geometry of **5** would therefore appear to have these atoms in a mutually *cis* arrangement. The retention of the bidentate coordination mode for the thiocarbamoyl ligand in this and the above reaction with NaBH_4 is noteworthy and indicates a considerable preference for such coordination, at least for low-valent ("soft") ruthenium(II). The contrasting geometries of **3** and **5** further support the intermediacy of a formyl complex in the reaction of 2^+ with borohydride. Were hydride addition to occur at a coordinatively unsaturated intermediate (either from decarbonylation or monodentate thiocarbamoyl coordination), the same regiochemistry would be expected for **4** as for **3**. However, direct addition of hydride to 2^+ would be expected to occur at the carbonyl ligand *trans* to the thiocarbamoyl carbon. Loss of the remaining carbonyl ligand must therefore be followed by a regioselective migration of the hydride to the site adjacent to the thiocarbamoyl carbon, consistent with the facility of $\text{Me}_2\text{NC}(\text{S})\text{H}$ elimination observed in the mass spectrum.

The reaction of $2 \cdot \text{PF}_6$ with sodium dimethyldithiocarbamate in refluxing ethanol resulted in the loss of a carbonyl and one phosphine ligand to give $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)]$ (**6**). This neutral complex exhibits a single ν_{CO} absorption at 1909 cm^{-1} (CH_2Cl_2) in addition to absorbances at 1553, 1529 (ν_{NC}), 1232 and 922 (ν_{CS}) cm^{-1} typical of the *dihapto* thiocarbamoyl ligand. The ^1H NMR has two singlets attributed to the thiocarbamoyl methyl groups at 2.95 and 3.07 ppm, whereas those assigned to the dimethyldithiocarbamate ligand appear at 3.28 and 3.41 ppm. The complex shows a singlet at 50.3 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum has doublet resonances for both the thiocarbamoyl and carbonyl carbons (243.9 and 205.2 ppm, respectively), confirming the coordination of only one phosphine. The dithiocarbamate carbon resonance occurs at 212.9 ppm and is a singlet, as are the four methyl groups. FAB-MS analysis reveals a significant molecular ion and also indicates that the dimethyldithiocarbamate unit is lost as a major fragment (much more readily than the bidentate thiocarbamoyl unit) along with the carbonyl and phosphine. The displacement of a phosphine in preference to the adoption of a *monohapto* thiocarbamoyl coordination is notable, given that the reaction of $[\text{Ru}(\text{SCSMe})(\text{CO})_2(\text{PPh}_3)_2]^+$ with $\text{Na}[\text{S}_2\text{CNET}_2]$ does indeed provide $[\text{Ru}\{\eta^1\text{-C}(\text{S})\text{SMe}\}(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2]$, a bis(phosphine) complex with a *monohapto* dithiomethoxycarbonyl ligand.^{29b} However, the reaction of the thioaroyl complex $[\text{Os}(\eta^2\text{-SCR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) with $\text{Na}[\text{S}_2\text{CNET}_2]$ does provide $[\text{Os}(\eta^2\text{-SCR})(\kappa^2\text{-S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)]$, albeit under forcing conditions (15 h, refluxing xylene and 2-methoxyethanol mixture).^{3e} The complex **6** is formally isoelectronic with the salt $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{NO})(\text{PPh}_3)]\text{PF}_6$ obtained via the oxidative addition of bis(dimethyldithiocarbamoyl)sulfide to $[\text{RuCl}(\text{NO})(\text{PPh}_3)_2]$.¹⁹ Accordingly, an alternative route to **6** is provided by the reaction of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ and $(\text{Me}_2\text{NCS})_2\text{S}$ in refluxing ethanol. The overall yield

for this method is superior to that for the two-step route as well as requiring a much shorter reaction time.

The isonitrile analogue of **2-Cl**, $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ (**7-Cl**), was prepared via the rapid reaction of $[\text{Ru}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})(\text{PPh}_3)_3]$ ³² with *N,N*-dimethylthiocarbamoyl chloride. Absorptions due to the isocyanide, carbonyl, and thiocarbamoyl ligands are all clearly visible in the infrared spectrum $[\text{CH}_2\text{Cl}_2: 2130 \nu_{\text{CN}}, 1963 \nu_{\text{CO}}, \text{and } 1590 \nu_{\text{NCl}} \text{ cm}^{-1}]$. All three groups give rise to triplet resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 236.3 (SC, $^2J_{\text{CP}} = 8.9 \text{ Hz}$), 203.5 (CO, $^2J_{\text{CP}} = 12.5 \text{ Hz}$), and 158.5 (NC, J_{CP} unresolved) ppm. In contrast to the carbonyl analogue, **7-Cl** does not undergo reaction with sodium borohydride. The reaction of $[\text{Ru}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})(\text{PPh}_3)_3]$ with bis-(thiocarbamoyl)sulfide led only to the isolation of **7·S₂CNMe₂** with $[\text{S}_2\text{CNMe}_2]^-$ as the counteranion, rather than ejection of a carbonyl ligand and formation of $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{PPh}_3)]$. The less π -acidic isonitrile ligand (cf. CO in **2⁺**) presumably allows stronger coordination of the single CO in **7⁺** than those in **2⁺**.

Rhodium Complexes. Known or claimed thiocarbamoyl complexes of rhodium^{19,34–39} are summarized in Scheme 5, including the structurally characterized examples $[\text{Rh}(\eta^2\text{-SCNMe}_2)(\text{PPh}_3)\{\text{HB}(\text{pz})_3\}]\text{Cl}$,³⁵ $[\text{Rh}_2\text{-Cl}_2(\text{CO})(\text{SCNMe}_2)(\text{dppm})_2]\text{BF}_4$,³⁶ $[\text{RhCl}(\text{SCNMe}_2)\{\text{SC}(\text{NMe}_2)\text{NPh}\}(\text{PPh}_3)]$,³⁷ and $[\text{RhCl}(\text{SCNMe}_2)(\text{S}_2\text{CNMe}_2)(\text{PPh}_3)]$,³⁸ for which pertinent data are reproduced in Table S1 (Supporting Information). All result from the oxidative addition of C–X bonds of $\text{Me}_2\text{NC}(\text{S})\text{X}$ (X = Cl, SMe, S₂CNMe₂, NPhCSNMe₂). The reaction of $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ with $\text{Me}_2\text{NC}(\text{S})\text{Cl}$ (6 h, 80 °C) has been reported to provide a red binuclear complex $[\text{Rh}_2(\mu\text{-Cl})_2(\eta^2\text{-SCNMe}_2)_2\text{Cl}_2(\text{PPh}_3)_4]$,³⁴ while a later report suggests a mononuclear structure.³⁹ We find that the reaction of $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ with Me_2NCSCl does indeed provide a neutral mononuclear red complex, $[\text{Rh}(\eta^2\text{-SCNMe}_2)\text{Cl}_2(\text{PPh}_3)_2]$ (**8**), the mononuclear formulation being confirmed by FAB mass spectrometry. In contrast with the iridium chemistry described below, it appears impossible to isolate a salt of the form $[\text{Rh}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ under the conditions necessary for any reaction to occur (refluxing tetrahydrofuran), as the carbonyl ligand is ejected thermally to give **8**. The same complex may be prepared by treating $\text{Me}_2\text{NC}(\text{S})\text{Cl}$ with the carbonyl-free precursor complex $[\text{RhCl}(\text{PPh}_3)_3]$ or $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+$ in good yields (Scheme 6). With these more reactive substrates, the reactions proceed readily at room temperature and **8** may be isolated in high yields (90–95%). Spectroscopic data for **8** are essentially

(32) This complex is an analogue of the known complex $[\text{Ru}(\text{CO})(\text{CNC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)_3]$.³³ It may be prepared using the analogous procedure by substituting $\text{CNC}_6\text{H}_4\text{Me-4}$ with the commercially available $\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6}$ (Aldrich).

(33) (a) Christian, D. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1271. (b) Grundy, K. R. *Inorg. Chim. Acta* **1981**, *53*, L225.

(34) Corain, B.; Martelli, M. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 39.

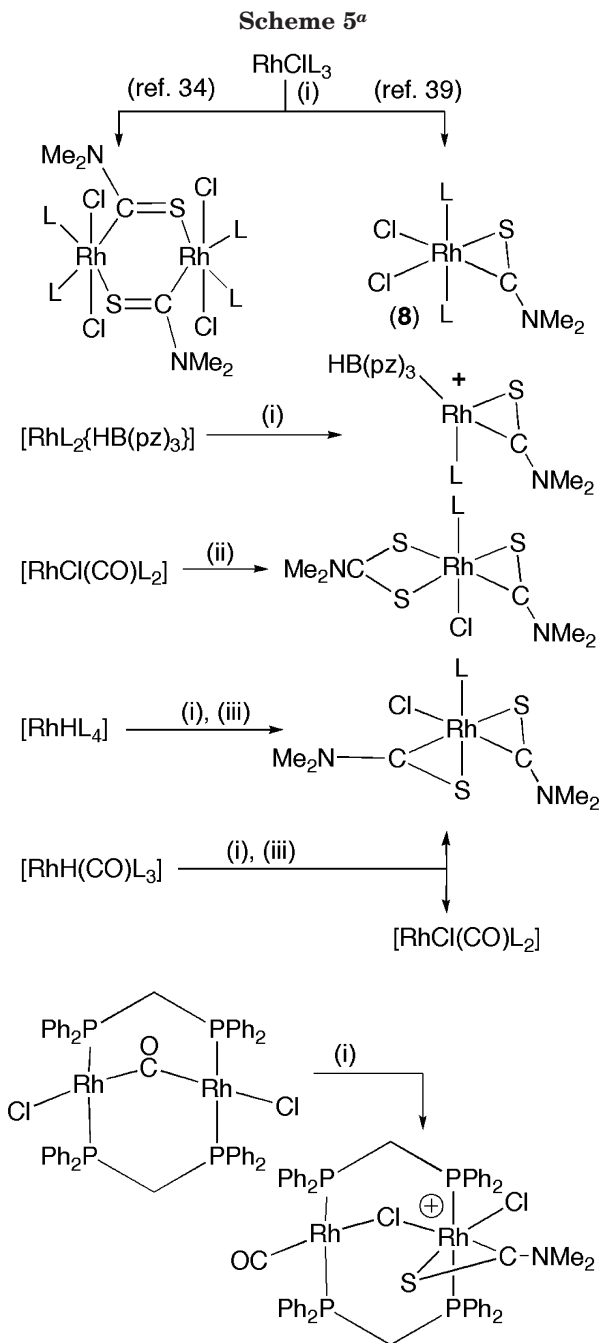
(35) Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. *T. Organometallics* **1998**, *17*, 3152.

(36) Gibson, J. A. E.; Cowie, M. *Organometallics* **1984**, *3*, 722.

(37) (a) Gal, A. W.; van der Ploeg, A. F. M. J.; Vollenbroek, F. A.; Bosman, W. *J. Organomet. Chem.* **1975**, *96*, 123. (b) Bosman, W. P.; Gal, A. W. *Cryst. Struct. Commun.* **1976**, *5*, 703.

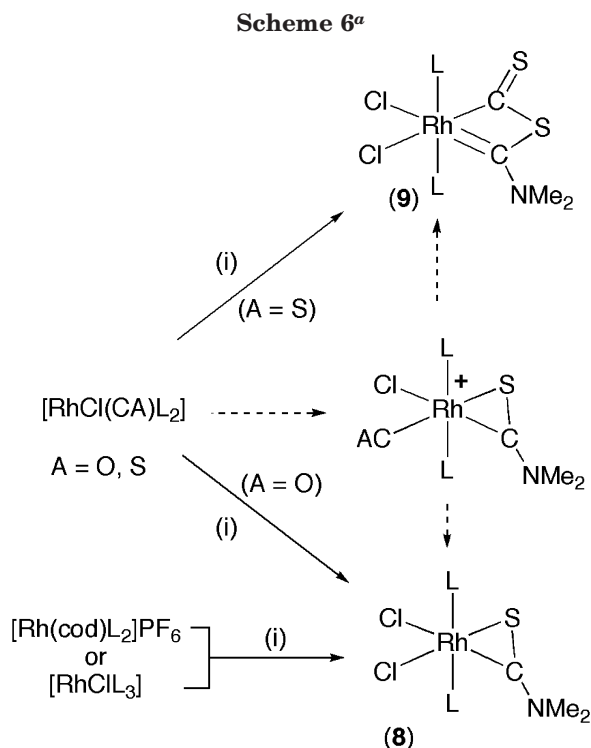
(38) Bosman, W. P.; Gal, A. W. *Cryst. Struct. Commun.* **1975**, *4*, 465.

(39) Gal, A. W.; Ambrosius, H. P. M. M.; van der Ploeg, A. F. M. J.; Bosman, W. P. *J. Organomet. Chem.* **1978**, *149*, 81.



analogous to those for the structurally characterized iridium analogue described below with the exceptions that the resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra appear as doublets due to coupling to rhodium.

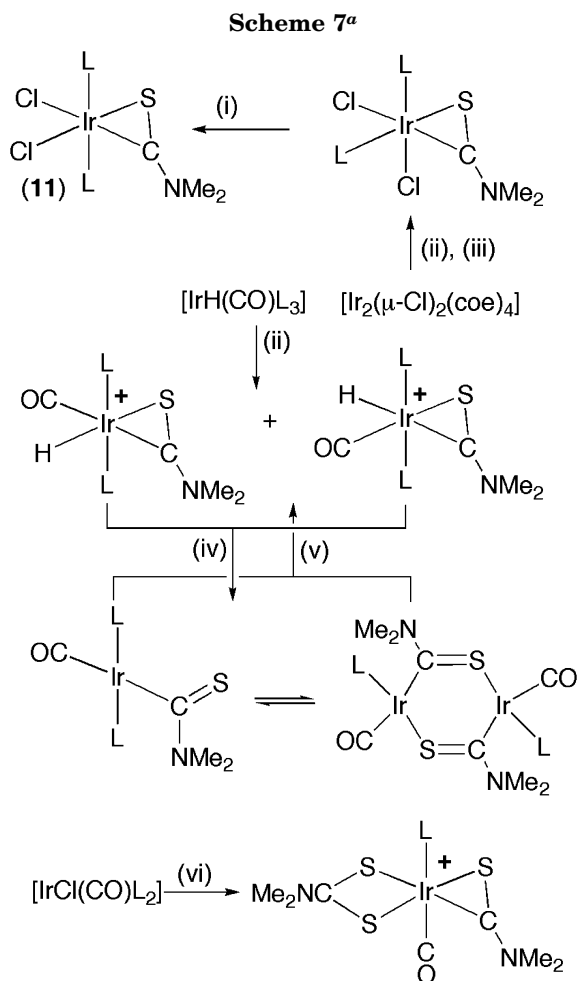
The difference in reactivity of the rhodium and iridium analogues extends also to the reactions of the species $[\text{MCl}(\text{CS})(\text{PPh}_3)_2]$ (M = Rh, Ir) with Me_2NCSCl (Scheme 4). Due to the strength of the M–CS bond, the formation of **8** by ejection of the thiocarbonyl ligand was considered unlikely. However, instead of providing the thiocarbonyl analogue of the elusive rhodium carbonyl complex, $[\text{Rh}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{Cl}$, a neutral yellow complex was isolated that did not display a characteristic ν_{CS} IR absorption for a terminal thiocarbonyl ligand (typically 1180–1380 cm^{-1}). A ν_{NC} stretch in the infrared spectrum (Nujol) at 1586 cm^{-1} and the presence of two methyl singlets in the ^1H NMR spec-



^a L = PPh₃, cod = 1,5-cyclooctadiene. (i) ClC(S)NMe₂.

trum at 2.33 and 2.43 ppm confirmed the presence of the thiocarbamoyl ligand. Due to the poor solubility of the complex in all available deuterated solvents, the ¹³C-{¹H} NMR spectrum could not be adequately recorded. The most diagnostic spectroscopic technique was found to be FAB mass spectrometry, which showed a series of fragmentations for a metallacycle formed by coupling of the thiocarbamoyl and thiocarbonyl ligands. We have found that the observation of the loss of a thiocarbonyl ligand in FAB mass spectrometry is very rare. Accordingly, isotopic distributions corresponding to [M - Cl - CS]⁺, [M - Cl - CS₂]⁺, [M - Cl - S₂CNMe₂]⁺, and [M - Cl - SCSCNMe₂]⁺ suggest the fragmentation of a metallacycle. Interestingly no molecular ion was seen, only a peak for [M - Cl]⁺ (*m/z* = 793); however the possibility of the complex being a chloride salt was rejected, as attempts to metathesize the chloride counteranion with KPF₆ failed. The formulation was further supported by elemental microanalysis. On the basis of this evidence, the product is tentatively formulated as [RhCl₂{κ²-C(NMe₂)SC(=S)}(PPh₃)₂] (**9**), as depicted in Scheme 6. There is a structural precedent for this class of metallacycle in the complex [OsH{κ²-C(NRMe)SC(S)}(PPh₃)₂] (R = C₆H₄CH₃-4), which was also obtained via the coupling of thiocarbamoyl and thiocarbonyl ligands, upon reaction of the complex [Os(η²-SCNRMe)(CO)(CS)(PPh₃)₂]⁺ with Na[BH₄].⁴⁰ Unfortunately, we were unsuccessful in obtaining crystals suitable for crystallographic analysis.

Iridium Complexes. Scheme 7 summarizes synthetic routes to known thiocarbamoyl complexes of iridium, which (as for rhodium) mainly rely on the oxidative addition of thiocarbamoyl chlorides or thiram. We have previously discussed the oxidative addition of chlorothionoformate and chlorodithiofor-



^aL = PPh₃, coe = cyclooctene. (i) CHCl₃, EtOH; (ii) ClCS-NMe₂; (iii) PPh₃; (iv) Et₃N; (v) HBF₄; (vi) S(CSNMe₂)₂.

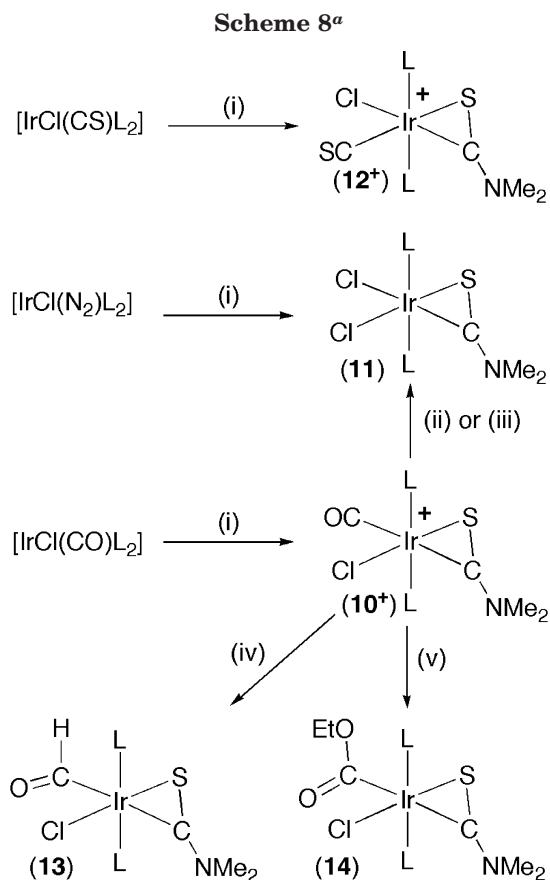
mates to Vaska's complex en route to the thiocarbonyl analogue of Vaska's complex [IrCl(CS)(PPh₃)₂].^{42a} Thus both [IrCl(CA)(PPh₃)₂] (A = O, S) react with ClCS₂Ph to provide the neutral dithiophenoxycarbonyl complexes [Ir{C(=S)SPh}Cl₂(CA)(PPh₃)₂], which on treatment with K[PF₆] provide the salts [Ir(η²-SCSPh)Cl(CA)(PPh₃)₂]-PF₆. In the preceding discussion, no evidence for the formation of monodentate thiocarbamoyl complexes had been obtained. We have therefore reinvestigated the reaction of [IrCl(CO)(PPh₃)₂] with Me₂NCSCl and extended it to the related reaction of [IrCl(CS)(PPh₃)₂] for comparison with the unexpected formation of **9** above. The reaction of Vaska's complex with Me₂NCSCl in refluxing benzene has been previously reported³⁹ to provide the salt [Ir(η²-SCNMe₂)Cl(CO)(PPh₃)₂]Cl (**10·Cl**), although the limited spectroscopic data do not unequivocally differentiate between this formulation and the neutral species [Ir{η¹-C(=S)NMe₂}Cl₂(CO)(PPh₃)₂], akin to [Ir{η¹-C(=S)SPh}Cl₂(CA)(PPh₃)₂].

A slow reaction ensues between [IrCl(CO)(PPh₃)₂] and Me₂NCSCl in dichloromethane at ambient temperatures (cf. that with ClCS₂Ph which is complete within 1 h).

(41) (a) Lu, G.-L.; Roper, W. R.; Wright, L. J.; Clark, G. R. *J. Organomet. Chem.* **2005**, *690*, 972. (b) Collins, T. J.; Roper, W. R.; Town, K. G. *J. Organomet. Chem.* **1976**, *121*, C41. (c) Kubota, K.; Carey, C. R. *J. Organomet. Chem.* **1970**, *29*, 491.

(42) (a) Hill, A. F.; Wilton-Ely, J. D. E. T. *Organometallics* **1996**, *15*, 5, 3791. (b) Hill, A. F.; Wilton-Ely, J. D. E. T. *Inorg. Synth.* **2002**, *33*, 244.

(40) Boniface, S. M.; Clark, G. R. *J. Organomet. Chem.* **1981**, *208*, 253.



However, heating the reagents in refluxing tetrahydrofuran under reflux leads to the spontaneous crystallization of the colorless product **10·Cl** (Scheme 8). The ionic formulation is further supported by the following observations: Metathesis of the counteranion (Cl⁻) with (NH₄)[PF₆] does not effect the solution spectroscopic data associated with the complex cation, excluding the alternative neutral formulation of [Ir{η¹-C(=S)NMe₂}-Cl₂(CO)(PPh₃)₂]. The gross molecular composition is also indicated by the appearance of a molecular ion at *m/z* = 868 showing the correct isotope distributions for the proposed formulation (although metal halide ionization is not uncommon in FAB mass spectrometry). In contrast to the proposed rhodium analogue which spontaneously decarbonylates, the salt **10·Cl** is thermally stable (thf or benzene reflux). However, it slowly converts (3–5 days) in bright sunlight at room temperature to give a neutral red species (Scheme 8), which shows no ν_{CO}-associated infrared absorption and gives rise to a molecular ion at *m/z* = 875 corresponding to [Ir(η²-SCNMe₂)Cl₂(PPh₃)₂] (**11**). Two isomers of this formulation have been suggested³⁹ as resulting from the subsequent treatment of [Ir₂(μ-Cl)₂(C₈H₁₄)₄] with triphenylphosphine and Me₂NCSCl. This species is however most conveniently prepared via the reaction of [IrCl(N₂)(PPh₃)₂] with Me₂NCSCl. In contrast to the reaction with [IrCl(CO)(PPh₃)₂], that with the dinitrogen complex is considerably more facile (30 min, CH₂Cl₂, 25 °C). It therefore seems likely that the mechanism is distinct, i.e., that the Me₂NCSCl displaces dinitrogen followed by oxidative addition rather than formation of the salt [Ir(η²-SCNMe₂)Cl(N₂)(PPh₃)₂]Cl. A third route to this

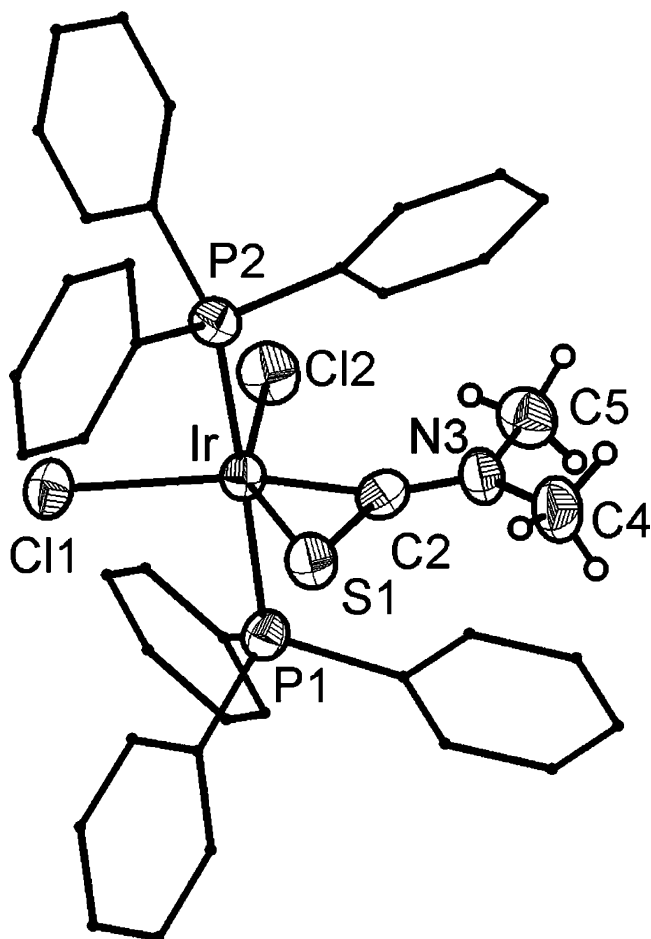


Figure 3. Molecular structure of [Ir(η²-SCNMe₂)Cl₂(PPh₃)₂] (**11**). (Phenyl groups simplified, 50% displacement ellipsoids.) Selected bond lengths (Å) and angles (deg): Ir–C2 = 1.971(6), Ir–P2 = 2.3594(19), Ir–P1 = 2.3652(19), Ir–Cl(2) = 2.3791(17), Ir–S1 = 2.4265(17), Ir–Cl(1) = 2.4823(17), S1–C2 = 1.704(7), C2–N3 = 1.279(8), P2–Ir–P1 = 177.49(7), C2–Ir–P2 = 90.3(2), C2–Ir–P1 = 90.4(2), C2–Ir–Cl(2) = 106.59(19), C2–Ir–S1 = 44.10(19), P2–Ir–Cl(1) = 88.97(6), P1–Ir–Cl(1) = 89.53(6), P2–Ir–Cl(2) = 90.52(7), P1–Ir–Cl(2) = 91.57(7), Cl(2)–Ir–Cl(1) = 93.19(6), P2–Ir–S1 = 88.71(6), P1–Ir–S1 = 90.14(6), S1–Ir–Cl(1) = 116.12(6), C2–S1–Ir = 53.6(2), S1–C2–Ir = 82.3(3), Cl(2)–Ir–S1 = 150.65(7), C2–Ir–Cl(1) = 160.21(19), C2–N3–C4 = 122.1(6), C2–N3–C5 = 122.2(6), C4–N3–C5 = 115.7(6).

complex is provided, somewhat surprisingly, by the slow reaction (16 h) of [Ir(η²-SCNMe₂)(CO)Cl(PPh₃)₂]Cl with HNMe₂ at room temperature. Given that two isomers have been reported for this complex on the basis of spectroscopic data, a crystal structure determination was carried out. Yellow platelike needles of [Ir(η²-SCNMe₂)Cl₂(PPh₃)₂]·2CH₂Cl₂ (**11**) were grown by layering ethanol on a saturated solution of the complex in dichloromethane. The results of the crystallographic study are summarized in Figure 3 and confirm (i) the *trans* bis(phosphine) arrangement and (ii) the *dihapto* coordination of the thiocarbamoyl ligand. The complex exhibits essentially an octahedral geometry with *cis*-interligand angles in the range 88.71(6)° to 116.12(6)°. As for **2·PF₆** and **3**, the thiocarbamoyl ligand, the metal, and the two remaining equatorial ligands are essentially coplanar. The two Ir–Cl bond lengths offer an internal comparison of the respective *trans* influences of the two

"ends" of the thiocarbamoyl ligand. The Ir–Cl2 bond which is "trans" to the sulfur is significantly (61 σ) shorter than that "trans" to C2, which is somewhat surprising for a pseudo-octahedral d⁶-center, if C2 and S1 are expected to have π -acid and π -donative character, respectively. Similarly, on steric grounds it might also be expected that Ir–Cl1 would be shorter.

The thiocarbonyl analogue of Vaska's complex, [Ir(CS)Cl(PPh₃)₂],^{41,42} behaved in a straightforward manner with Me₂NC(S)Cl, reacting to give [Ir(η^2 -SCNMe₂)-Cl(CS)(PPh₃)₂]Cl (**12**·Cl), with no indication of coupling of the thiocarbonyl and thiocarbamoyl ligands, in contrast to the formation of **9**. The thiocarbonyl ligand gave rise to a ν_{CS} absorption at 1349 cm⁻¹ in the infrared spectrum (Nujol), consistent with coordination to iridium(III), and a triplet at 254.5 (²J_{CP} = 8.1 Hz) ppm in the ¹³C{¹H} NMR spectrum. The thiocarbamoyl ligand exhibited a ν_{NC} band at 1616 cm⁻¹ in the IR spectrum (Nujol) and a triplet at 195.2 (²J_{CP} = 3.6 Hz) ppm in the ¹³C{¹H} NMR spectrum further upfield from that of the thiocarbonyl carbon. The reaction of [IrCl(CS)(PPh₃)₂] with PhSC(=S)Cl has been reported to give the neutral complex [Ir{ η^1 -C(=S)SPh}Cl₂(CS)(PPh₃)₂] if carried out in benzene,^{42a} but the salt [Ir(η^2 -SCSPh)Cl₂(CS)(PPh₃)₂]-PF₆ is obtained if the reaction is carried out in a mixture of CH₂Cl₂ and EtOH in the presence of KPF₆. Spectroscopic data for the latter are generally similar to those for **12**·Cl with the exception of the ¹³C resonance attributable to the dithioalkoxycarbonyl carbon, which appears at 250.9 ppm. The other feature that distinguishes these two reactions is the enhanced preference for *dihapto* coordination demonstrated by the thiocarbamoyl ligand relative to the dithioalkoxycarbonyl ligand in that no evidence for the formation of neutral complex [IrCl₂{ η^1 -C(=S)NMe₂}(CS)(PPh₃)₂] was obtained.

Colorless crystals of **12**·Cl(CHCl₃)₆ suitable for crystallography were grown from chloroform as a chloroform hexasolvate. The results of a crystallographic analysis are summarized in Figure 4. The geometry at the metal center is distorted octahedral (Figure 4) with *cis*-interligand angles ranging from 86.38(9)° to 111.92(11)°. An unusual feature of the crystal structure was the octahedral arrangement of the six chloroform molecules around the chloride counteranion (Figure 4b, average Cl₃CH...Cl = 2.55 Å).

The complex [IrH(η^2 -SCNMe₂)(CO)(PPh₃)₂]Cl has been previously prepared from the reaction of Me₂NC(S)Cl with [IrH(CO)(PPh₃)₃],³⁹ while the reaction of [Ir(SCSMe)Cl(CO)(PPh₃)₂]OTf with Na[BH₄] provides [IrH{C(=S)SMe}Cl(CO)(PPh₃)₂].⁴¹ It might therefore be expected that the reaction of **10**·Cl with ethanolic sodium borohydride would provide one or both of [IrH(η^2 -SCNMe₂)(CO)(PPh₃)₂]Cl and [IrHCl{C(=S)NMe₂}(CO)(PPh₃)₂]. In practice, neither is obtained; instead the reaction led to the isolation of the formyl complex [Ir(η^2 -SCNMe₂){ η^1 -C(=O)H}Cl(PPh₃)₂] (**13**). The presence of the formyl ligand was clearly indicated in the IR spectrum (Nujol) by a characteristic absorption at 2572 cm⁻¹ as well as the conspicuous absence of an absorption due to a terminal carbonyl ligand. A triplet resonance was observed at 14.67 (³J_{HP} = 6.6 Hz) ppm in the ¹H NMR spectrum, while a proton-coupled ¹³C NMR spectrum revealed the formyl resonance to be split

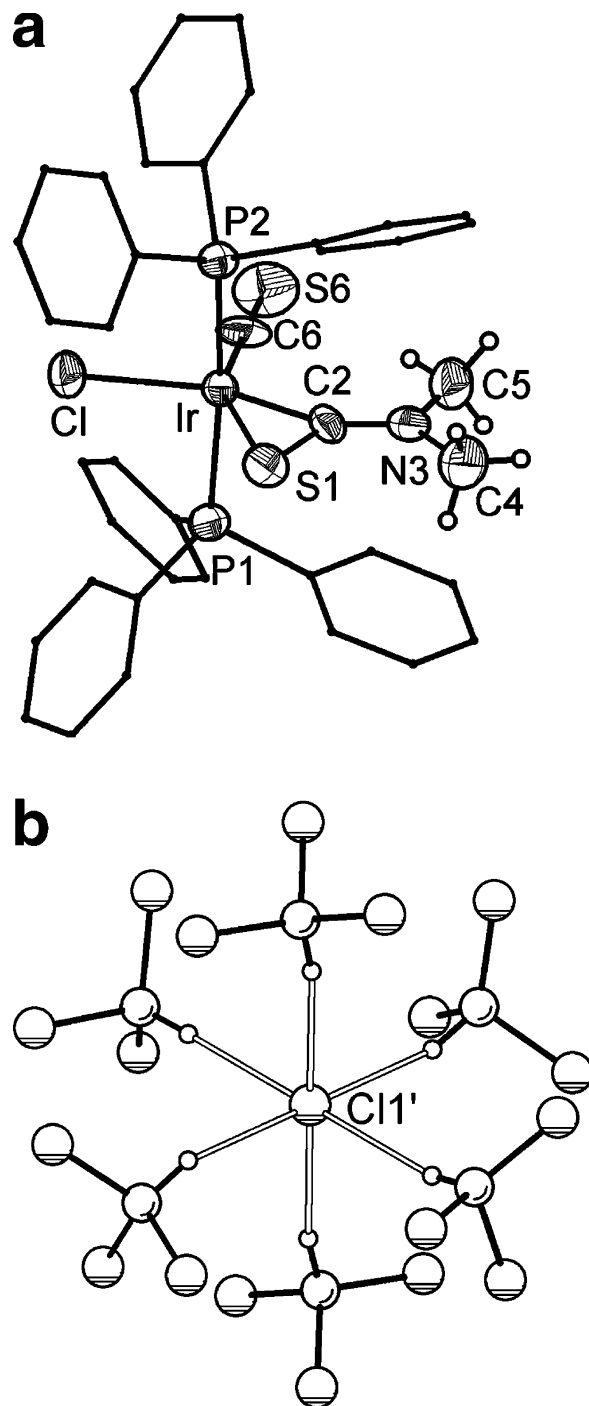


Figure 4. (a) Molecular structure of the cationic complex [Ir(η^2 -SCNMe₂)Cl(CS)(PPh₃)₂]⁺ (**12**⁺) in a crystal of **12**·Cl·(CHCl₃)₆. (Phenyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ir–C6 = 1.864(11), Ir–C2 = 1.994(11), Ir–P2 = 2.399(2), Ir–P1 = 2.402(2), Ir–Cl = 2.429(3), Ir–S1 = 2.491(3), S1–C2 = 1.669(11), C2–N3 = 1.288(13), P2–Ir–P1 = 173.42(10), C6–Ir–C2 = 109.3(5), C6–Ir–P2 = 93.0(3), C2–Ir–P2 = 90.9(3), C6–Ir–P1 = 92.4(3), C2–Ir–P1 = 90.7(3), C6–Ir–Cl = 96.9(4), P2–Ir–Cl = 86.38(9), P1–Ir–Cl = 89.33(10), C2–Ir–S1 = 41.9(3), P2–Ir–S1 = 88.79(9), P1–Ir–S1 = 88.19(9), Cl–Ir–S1 = 111.92(11), C2–Ir–Cl 153.8(3), C6–Ir–S1 151.2(4), C2–S1–Ir = 52.9(4), S1–C2–Ir = 85.2(5), C2–N3–C5 = 123.9(10), C2–N3–C4 = 119.9(11), C5–N3–C4 = 116.2(10). (b) Structure of the anionic complex [Cl(HCCl₃)₆]⁻ in a crystal of **12**·Cl·(CHCl₃)₆. (Chloroform molecules exhibit disorder; one orientation shown for each.)

into a doublet of triplets at 215.2 [$J_{\text{HC}} = 164.2$, $J_{\text{CP}} = 5.4$ Hz] ppm due to coupling to both the formyl proton and the mutually *trans* phosphorus nuclei. The thiocarbamoyl resonance in this spectrum appears as a somewhat broadened singlet at 205.3 ppm. The FAB mass spectrum showed fragmentations for the molecular ion at 868 (100), $[\text{M} - \text{HCO} - \text{PPh}_3]^+$ at 578 (41) and $[\text{M} - \text{Cl} - \text{HCO} - \text{PPh}_3]^+$ at 542 (33). Unfortunately, crystals of suitable quality for a crystallographic analysis were not obtained. Although formyl complexes of group 8 metals have been well-studied,^{43–47} very few formyl complexes of group 9 metals are known,^{47,48} but do include a rare example of a thioformyl complex $[\text{Ir}\{\text{C}(\text{S})\text{H}\}\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]^{3a}$ and the structurally characterized salt $[\text{IrH}\{\text{C}(\text{O})\text{H}\}(\text{PMe}_3)_4]\text{PF}_6$.⁴⁸

The carbonyl ligand in $\mathbf{10}^+$ has ν_{CO} 2042 cm^{-1} ($\text{CH}_2\text{-Cl}_2$), and accordingly it is perhaps not surprising that this ligand would be prone toward nucleophilic attack. What is unexpected, however, is that the formyl complex is stable and does not decompose via transfer of the hydrogen to the metal, as is generally the case for formyls. Such an α -Ir-H elimination would require a vacant coordination site on iridium, and thus the stability of $\mathbf{13}$ may be taken as testament to the tenacity of the *dihapto* thiocarbamoyl coordination.

To investigate further the reaction of nucleophiles at the carbonyl ligand, $\mathbf{10}\cdot\text{Cl}$ was treated with sodium ethoxide in ethanolic solution to provide rapidly the ethoxycarbonyl species $[\text{Ir}(\eta^2\text{-SCNMe}_2)\{\eta^1\text{-C}(\text{O})\text{OEt}\}\text{Cl}(\text{PPh}_3)_2]$ ($\mathbf{14}$). The ethyl group was observed in the ^1H NMR spectrum as a triplet resonance at 0.66 ($J_{\text{HH}} = 7.3$ Hz) ppm and a quartet at 3.57 ($J_{\text{HH}} = 7.3$ Hz) ppm. The ethoxycarbonyl group gave rise to a ν_{OCO} absorption at 1618 cm^{-1} in the IR spectrum (Nujol) and resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum: a triplet at 168.3 ($J_{\text{CP}} = 6.3$ Hz) and singlets at 59.8 and 14.1 ppm for the ethyl carbons, respectively. Attempts at preparing a carbamoyl thiocarbamoyl species by nucleophilic attack of lithium diisopropylamide and secondary amines proved unsuccessful. As noted above, dimethylamine leads to slow decarbonylation to provide $\mathbf{11}$, and since this reaction does not proceed in the absence of amine, it may be surmised that the amine does indeed attack the carbonyl but that the resulting carbamoyl complex is unstable.

Concluding Remarks

Convenient general synthetic routes to thiocarbamoyl complexes of divalent ruthenium and trivalent rhodium and iridium have been illustrated, and reactivity studies

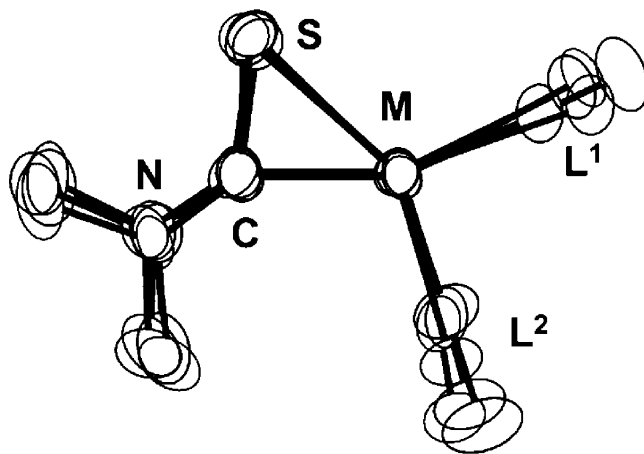


Figure 5. Superposition of the equatorial planar sections of the molecular structures of the complexes $\mathbf{2}^+$, $\mathbf{3}$, $\mathbf{11}$, and $\mathbf{12}^+$ (50% displacement ellipsoids).

indicate that the bidentate-*C,S* coordination mode is strongly favored and ultimately retained in co-ligand modification reactions. In the case of the salt $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ ($\mathbf{10}\cdot\text{Cl}$), the reactivity of the species is centered on the carbonyl ligand (CH_2Cl_2 : ν_{CO} 2042 cm^{-1}), thus providing compounds bearing both thiocarbamoyl and formyl or alkoxycarbonyl ligands. A representative series of examples has been investigated crystallographically. Table S1 (Supporting Information) collates pertinent geometrical parameters for the 22 structurally characterized “metallathiirenes” of ruthenium, osmium, and iridium,^{3,5,18,29,35–38,49–51} including the complexes $\mathbf{2}^+$, $\mathbf{3}$, $\mathbf{11}$, and $\mathbf{12}^+$. Remarkably, there is very little obvious correlation between the geometric parameters M–C, M–S, C–S, and M–C–S. Furthermore, Figure 5 depicts a superposition of the equatorial planes of the complexes $\mathbf{2}^+$, $\mathbf{3}$, $\mathbf{11}$, and $\mathbf{12}^+$ and again, to the naked eye, there is little notable variation in the orientations of either the thiocarbamoyl or the two remaining ligands. This comparative lack of geometric flexibility coupled with the paucity of reactions involving the thiocarbamoyl ligand itself might point to such ligands serving as useful three-electron spectator ligands, were it not for the observation of a novel coupling of thiocarbamoyl and thiocarbonyl ligands observed in the formation of $\mathbf{9}$. In the context of other more common three-electron ligands, consideration of the IR data in Table 1 leads to the conclusion that the thiocarbamoyl ligand is a comparatively strong net donor, given the popular convention of describing the metal centers in the nitrosyl and alkylidyne complexes as formally zerovalent.

Experimental Section

General Comments. Unless otherwise stated, all manipulations were carried out under aerobic conditions using commercially available solvents and reagents as received. Infrared and NMR spectroscopy was carried out at 25 °C using Perkin-Elmer 1720-X and JEOL JNM EX270 spectrometers, respectively. “*t*” implies a virtual triplet, taken as evidence of mutually *trans*-coordinated phosphine ligands. Generally the resonances for the *ortho* and *meta* carbon nuclei of PPh_3 ligands were not unequivocally distinguished, having comparable J_{PC} values. FAB mass spectra (nitrobenzyl alcohol matrixes) were measured using an Autospec Q instrument; for salts, “M” refers to the cationic complex. All solid-state

(43) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089.

(44) (a) Casey, C. P.; Meszaros, M. W.; Neumann, S. M.; Gennick-Cesa, I.; Haller, K. *J. Organometallics* **1985**, *4*, 143. (b) Casey, C. P.; McAlister, D. R.; Calabrese, J. C.; Neumann, S. M.; Andrews, M. A.; Meszaros, M. W.; Haller, K. *J. Cryst. Struct. Commun.* **1982**, *11*, 1015;

(45) (a) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335. (b) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (c) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.

(46) (a) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 387. (b) Nelson, G. O.; Sumner, C. E. *Organometallics* **1986**, *5*, 1983.

(47) (a) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (b) Wayland, B. B.; Woods, B. A. *Chem. Commun.* **1981**, 700.

(48) Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109.

infrared samples were measured as Nujol mulls between KBr plates. Elemental microanalytical data were provided by SACS at London Metropolitan University. The FT-Raman spectrum of **4** was provided by Dr. E. Coleyshaw. Petroleum ether refers to the fraction that boils between 40 and 60 °C. The complex $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ was prepared as described below, with minor modifications to the method described by Roper²⁸ that avoid the use of silver salts, residual traces of which compromise the storage properties. The complex $[\text{Ru}(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)(\text{CO})(\text{PPh}_2)_3]$ ⁵² is an analogue of $[\text{Ru}(\text{CNC}_6\text{H}_4\text{Me}-4)(\text{CO})(\text{PPh}_3)_3]$ described previously³³ and may be prepared using either of the reported multistep procedures, substituting $\text{CNC}_6\text{H}_4\text{Me}-4$ with commercially available $\text{CNC}_6\text{H}_3\text{Me}_2-2,6$. The remaining complexes $[\text{Ru}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2]$,²⁹ $[\text{RhCl}(\text{PPh}_3)_3]$,⁵³ $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$,⁵⁴ $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$,⁵⁵ $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$,⁵⁶ $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$,⁵⁷ $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$,⁵⁸ and $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ ⁵⁹ were prepared according to published procedures. Various procedures are available for the preparation of $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$,^{41,42,55} of which we used that described in ref 42b, with the modification that the amount of hydrochloric acid used in the penultimate step was doubled. All other reagents were used as received from commercial sources.

Preparation of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (1**).** A mixture of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (2.00 g, 2.10 mmol) and sodium tetrafluoroborate (1.84 g) was heated in refluxing acetonitrile (60 mL) for 40 min. The hot solution was filtered through diatomaceous earth and the filtrate transferred to a 250 mL round-bottomed flask and freed of volatiles (rotary evaporator). Dichloromethane (100 mL) was added to the residue, and carbon monoxide was then bubbled through the mixture for 5 min. The flask was sealed under an atmosphere of carbon monoxide, and the contents were stirred vigorously for 1 h. After this time the extent of the conversion to $[\text{RuH}(\text{CO})_2(\text{NCMe})(\text{PPh}_3)_2]\text{-BF}_4$ was determined by solution infrared spectroscopy ($\text{CH}_2\text{-Cl}_2$), and if necessary, further carbon monoxide was passed through the mixture. The dichloromethane was then removed (rotary evaporator) and to the residue were added triphenylphosphine (1.00 g) and potassium hydroxide pellets (0.7 g). Dry, degassed methanol (50 mL) was added and the suspension heated anaerobically under reflux for 20 min and then filtered while hot. The bright yellow precipitate was washed with methanol (2×50 mL) and then dried under vacuum. Yield: 1.55 g (78%). The material obtained by this method was suitable for subsequent synthetic applications, although it can be recrystallized from dichloromethane and ethanol under strictly anaerobic conditions in the event that traces of KBF_4 (IR) remain. Note: Extended reflux times or the use of ethanol in the final step results in appreciable contamination with $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$. Carbonyl-associated infrared data for $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$, $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$, and **1** are sufficiently similar that these alone are insufficient to determine purity. $^{31}\text{P}\{^1\text{H}\}$ NMR data are, however, definitive.

(49) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Organometallics* **1992**, *11*, 3931.

(50) Attar-Bashi, M. T.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J.; Woodgate, S. D. *Organometallics* **1998**, *17*, 504.

(51) Dean, W. K. *Cryst. Struct. Commun.* **1979**, *8*, 335.

(52) Herberhold, M.; Hill, A. F. *J. Organomet. Chem.* **1989**, *368*, 111.

(53) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 77.

(54) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 79.

(55) Kubota, M.; Ho, C. O. M. *Inorg. Synth.* **1979**, *19*, 204.

(56) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816.

(57) Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1990**, *28*, 92.

(58) Collman, J. P.; Hoffman, N. W.; Hosking, J. W. *Inorg. Synth.* **1970**, *12*, 8.

(59) Laing, K. R.; Roper, W. R. *J. Chem. Soc. A* **1970**, 2149.

(60) Roper, W. R. In *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; NATO ASI Series C, Vol. 392; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993.

(61) Johnson, B. F. G.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1973**, 478.

(62) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2748.

Preparation of $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\text{CO})_2(\text{PPh}_3)_2]\text{Cl}$ (**2-Cl**).

(a) This reaction must be carried out under strictly anaerobic conditions due to the air-sensitivity of **1**; however the subsequent workup may be carried out aerobically. *N,N*-Dimethylthiocarbamoyl chloride (0.27 g, 2.15 mmol) and $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**1**: 1.00 g, 1.06 mmol) were combined in a Schlenk tube under nitrogen. To this was added thoroughly dried and degassed tetrahydrofuran (50 mL) and the mixture stirred for 1 h. Addition of petroleum ether (80 mL) completed precipitation of the colorless product, which may be recrystallized from a mixture of dichloromethane and ethanol. Yield: 0.80 g (94%). (b) $[\text{Ru}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (0.20 g, 0.26 mmol) and *N,N*-dimethylthiocarbamoyl chloride (0.07 g, 0.57 mmol) were dried under vacuum and dissolved in dried and degassed tetrahydrofuran (30 mL), and the mixture was stirred for 2 h. Addition of petroleum ether (50 mL) completed precipitation of the colorless product. Yield: 0.16 g (75%). The less soluble hexafluorophosphate salt (**2-PF₆**) was prepared by metathesis of **2-Cl** in dichloromethane with a solution of $[\text{NH}_4]\text{PF}_6$ in water and ethanol. IR CH_2Cl_2 : 2048, 1988 ν_{CO} , 1602 ν_{NC} cm^{-1} . Nujol: 2052, 1989 ν_{CO} , 1599 ν_{NC} , 1309, 1219, 916 ν_{CS} , 816 cm^{-1} . NMR (CDCl_3 , 25 °C) ^1H : 2.42, 2.83 (s \times 2, 6 H, CH_3), 7.25–7.60 (m, 30 H, C_6H_5) ppm. $^{13}\text{C}\{^1\text{H}\}$: 231.1 (t, CS, $^2J_{\text{CP}} = 8.9$), 199.9 (t, CO, $^2J_{\text{CP}} = 11.6$), 199.4 (t, CO, $^2J_{\text{CP}} = 12.5$), 133.5 (t^v, o/m- C_6H_5 , $J_{\text{CP}} = 5.4$), 131.8 (p- C_6H_5), 129.8 (t^v, i- C_6H_5 , $J_{\text{CP}} = 25.0$), 129.1 (t^v, o/m- C_6H_5 , $J_{\text{CP}} = 5.4$ Hz), 49.1, 48.0 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$: 33.7 ppm. FAB-MS *m/z* (% abundance): 770 (75) $[\text{M}]^+$, 742 (100) $[\text{M} - \text{CO}]^+$, 480 (23) $[\text{M} - \text{CO} - \text{PPh}_3]^+$, 452 (15) $[\text{M} - 2\text{CO} - \text{PPh}_3]^+$, 407 (3) $[\text{M} - 2\text{CO} - \text{PPh}_3 - \text{NMe}_2]^+$. Anal. (**2-PF₆**) Found: C, 50.3; H, 4.0; N, 1.4. $\text{C}_{41}\text{H}_{36}\text{F}_6\text{N}_2\text{O}_2\text{P}_3\text{RuS}$ requires: C, 50.5; H, 3.8; N, 1.4. *Crystal data for 2-PF₆*: $\text{C}_{42}\text{H}_{37}\text{Cl}_3\text{F}_6\text{N}_2\text{O}_2\text{P}_3\text{RuS}$, $M_w = 1034.12$, triclinic, $P\bar{1}$ (#2), $a = 13.062(4)$ Å, $b = 14.194(7)$ Å, $c = 15.229(4)$ Å, $\alpha = 66.88(3)^\circ$, $\beta = 70.28(2)^\circ$, $\gamma = 63.82(3)^\circ$, $V = 2283.8(14)$ Å³, $Z = 2$, $\mu(\text{Cu K}\alpha) = 6.340$ mm^{-1} , $D_{\text{calc}} = 1.504$ Mg m^{-3} , $T = 293(2)$ K, colorless plate, 6343 independent measured reflections, $R_1 = 0.0473$, $wR_2 = 0.1203$, 5045 absorption-corrected reflections [$I > 2\sigma(I)$], $2\theta \leq 116^\circ$], 555 parameters, CCDC 275850.

Preparation of $[\text{Ru}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (**3**) (**CO trans to S**).

A suspension of $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\text{CO})_2(\text{PPh}_3)_2]\text{Cl}$ (**2-Cl**: 0.20 g, 0.25 mmol) in ethanol (20 mL) was heated under reflux for 6 h and then allowed to cool to room temperature. The product was isolated by filtration, washed with petroleum ether (20 mL), and dried under vacuum. Yield: 0.19 g (95%). The complex was identified by comparison of spectroscopic data with those previously published for **3**, prepared via an alternative route.²⁰ A sample for crystallographic analysis was grown from chloroform as a monosolvate. *Crystal data for 3-CHCl₃*: $\text{C}_{41}\text{H}_{37}\text{Cl}_4\text{NOP}_2\text{RuS}$, $M_w = 896.59$, monoclinic, $P2_1/n$, $a = 17.314(2)$ Å, $b = 9.4199(10)$ Å, $c = 25.059(3)$ Å, $\beta = 92.716(8)^\circ$, $V = 4082.5(8)$ Å³, $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.808$ mm^{-1} , $D_{\text{calc}} = 1.459$ Mg m^{-3} , $T = 293(2)$ K, pale yellow block, 7178 independent measured reflections, $R_1 = 0.0792$, $wR_2 = 0.1692$, 3231 independent absorption-corrected reflections [$I > 2\sigma(I)$], $2\theta \leq 50^\circ$], 450 parameters, CCDC 275851.

Preparation of $[\text{RuH}(\eta^2\text{-SCNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ (**4**).

A solution of $[\text{Ru}(\eta^2\text{-SCNMe}_2)(\text{CO})_2(\text{PPh}_3)_2]\text{Cl}$ (**2-Cl**: 1.00 g, 1.24 mmol) in a mixture of dichloromethane (100 mL) and ethanol (60 mL) was treated with a filtered solution of sodium borohydride (0.50 g, 13.2 mmol, excess) in ethanol (50 mL). The resulting suspension was stirred for 1 h and then filtered to provide the pale green product, which was washed successively with water (40 mL), ethanol (40 mL), and petroleum ether (40 mL) and then dried under vacuum. Yield: 0.90 g (98%). The crude product could be recrystallized from a mixture of dichloromethane and ethanol. IR CH_2Cl_2 : 1912 ν_{CO} , 1561 ν_{NC} cm^{-1} . Nujol: 1905 ν_{CO} , 1557 ν_{NC} , 1308, 1230, 920 ν_{CS} , 832 cm^{-1} (ν_{RuH} not unambiguously identified). Raman: 1913 ν_{CO} cm^{-1} . NMR (CDCl_3 , 25 °C) ^1H : -14.27 (t, 1 H, RuH , $^2J_{\text{HP}} = 22.1$ Hz), 1.77, 2.64 (s \times 2, 6 H, CH_3), 7.20–7.65 (m, 30 H, C_6H_5) ppm. $^{13}\text{C}\{^1\text{H}\}$: 256.7 (t, CS, $^2J_{\text{CP}} = 11.6$), 210.6 (t, CO,

$^2J_{CP} = 15.2$), 136.8 (t ν , *i*-C₆H₅, $J_{CP} = 20.6$), 134.3 (t ν , *o*/m-C₆H₅, $J_{CP} = 6.3$), 129.1 (p-C₆H₅), 127.5 (t ν , *o*/m-C₆H₅, $J_{CP} = 4.5$ Hz), 45.7, 43.7 (CH₃) ppm. $^{31}P\{^1H\}$: 48.9 ppm. FAB-MS *m/z* (% abundance): 742 (5) [M]⁺, 655 (3) [M - SCNMe₂]⁺, 625 (2) [M - SCNMe₂ - CO]⁺, 480 (3) [M - PPh₃]⁺, 452 (3) [M - CO - PPh₃]⁺, 363 (4) [RuPPh₃]⁺. Anal. Found: C, 59.7; H, 4.9; N, 1.7. C₄₀H₃₇NOP₂RuS·CH₂Cl₂ requires: C, 59.5; H, 4.8; N, 1.7 (CH₂Cl₂ by 1H NMR integration).

Preparation of [Ru(η^2 -SCNMe₂)Cl(CO)(PPh₃)₂] (5) (CO *cis* to S). To a solution of [RuH(η^2 -SCNMe₂)(CO)(PPh₃)₂] (4: 0.30 g, 0.40 mmol) in dichloromethane (20 mL) and ethanol (15 mL) was added a solution of concentrated hydrochloric acid (3 drops) in ethanol (10 mL). The mixture was stirred for 1 h. Concentration of the solution (rotary evaporator) provided a yellow product, which was isolated by filtration and washed with water (10 mL), ethanol (20 mL), and petroleum ether (20 mL). Yield: 0.20 g (64%). The product could be recrystallized from a mixture of dichloromethane and ethanol. IR CH₂Cl₂: 1957 ν_{CO} , 1560 ν_{NC} cm⁻¹. Nujol: 1940 ν_{CO} , 1562 ν_{NC} , 1313, 941 ν_{CS} , 830 cm⁻¹. NMR (CDCl₃, 25 °C) 1H : 2.49, 2.65 (2 \times s, 6 H, CH₃), 7.10–8.00 (m, 30 H, C₆H₅) ppm. $^{31}P\{^1H\}$: 22.0 ppm. FAB-MS *m/z* (% abundance): 778 (28) [M]⁺, 749 (4) [M - CO]⁺, 742 (4) [M - Cl]⁺, 689 (82) [M - SCNMe₂]⁺, 654 (8) [M - SCNMe₂ - Cl]⁺, 625 (20) [Ru(PPh₃)₂]⁺, 487 (8) [M - CO - PPh₃]⁺, 452 (20) [M - Cl - CO - PPh₃]⁺, 363 (26) [RuPPh₃]⁺. Anal. Found: C, 56.3; H, 4.4; N, 1.6. C₄₀H₃₆ClNOP₂RuS·1.25CH₂Cl₂ requires: C, 56.1; H, 4.4; N, 1.6 (CH₂Cl₂ by 1H NMR integration).

Preparation of [Ru(η^2 -SCNMe₂)(κ^2 -S₂CNMe₂)(CO)-(PPh₃)₂] (6). (a) [Ru(η^2 -SCNMe₂)(CO)₂(PPh₃)₂]PF₆ (2·PF₆) (0.20 g, 0.22 mmol) was suspended in ethanol (30 mL) and NaS₂CNMe₂ (0.13 g, 0.91 mmol, excess) added as a solution in water (2 mL) and ethanol (10 mL). The reaction mixture was then heated under reflux for 24 h. The solvent was removed under reduced pressure and the residue extracted into toluene (50 mL) and filtered through diatomaceous earth to remove any ionic contaminants. The toluene was then removed from the filtrate and the residue crystallized from dichloromethane (20 mL) and ethanol (20 mL) by slow concentration (rotary evaporator) to provide pale yellow crystals. Yield: 0.12 g (92%). (b) A suspension of [Ru(CO)₂(PPh₃)₃] (1: 0.15 g, 0.16 mmol) and [S(SCNMe₂)₂] (0.04 g, 0.19 mmol) in degassed ethanol (20 mL) was heated at reflux for 3 h under nitrogen. The resultant pale yellow product was filtered, washed with ethanol (20 mL) and hexane (20 mL), and dried. Yield: 0.09 g (95%). IR CH₂-Cl₂: 1909 ν_{CO} , 1561, 1520 ν_{NC} cm⁻¹. Nujol: 1908 ν_{CO} , 1553, 1529 ν_{NC} , 1393, 1307, 1257, 1232, 1181, 1152, 922 ν_{CS} , 842 cm⁻¹. NMR (CDCl₃, 25 °C) 1H : 2.95, 3.07 [s \times 2, 6 H, SCN-(CH₃)₂], 3.28, 3.41 [s \times 2, 6 H, S₂CN(CH₃)₂], 7.25–7.80 (m, 15 H, C₆H₅) ppm. $^{13}C\{^1H\}$: 243.9 (d, SCNMe₂, $^2J_{CP} = 8.9$), 212.9 (S₂CNMe₂), 205.2 (d, CO, $^2J_{CP} = 14.2$), 134.3 (d, *i*-C₆H₅, $^1J_{CP} = 44.6$), 133.7 (d, *o*/m-C₆H₅, $J_{CP} = 10.7$), 129.9 (p-C₆H₅), 128.0 (d, *o*/m-C₆H₅, $J_{CP} = 9.0$ Hz), 46.9, 45.6 [(SCN(CH₃)₂)], 38.9 [S₂-CN(CH₃)₂] ppm. $^{31}P\{^1H\}$: 50.3 ppm FAB-MS *m/z* (% abundance): 600 (7) [M]⁺, 572 (11) [M - CO]⁺, 482 (4) [M - SCNMe₂ - CO]⁺, 309 (17) [M - CO - PPh₃]⁺. Anal. Found: C, 49.9; H, 4.0; N, 4.4. C₂₅H₂₇N₂OPRuS₃ requires: C, 50.1; H, 4.5; N, 4.7.

Preparation of [Ru(η^2 -SCNMe₂)(CNC₆H₃Me₂-2,6)(CO)-(PPh₃)₂]Cl (7·Cl). [Ru(CNC₆H₃Me₂-2,6)(CO)(PPh₃)₃] (0.30 g, 0.29 mmol) and Me₂NC(S)Cl (0.07 g, 0.57 mmol) were dried under vacuum and dissolved in degassed tetrahydrofuran (25 mL). The orange suspension was stirred for 3 h at room temperature, resulting in the formation of a colorless product. This was filtered and washed with petroleum ether (35 mL) and dried. Yield: 0.23 g (88%). The product can be recrystallized from chloroform and ethanol. IR CH₂Cl₂: 2130 $\nu_{C=N}$, 1963 ν_{CO} , 1590 ν_{NC} cm⁻¹. Nujol: 2125 $\nu_{C=N}$, 1947 ν_{CO} , 1592 ν_{NC} , 1311, 1222, 1172, 917, 827 cm⁻¹. NMR (CDCl₃, 25 °C) 1H : 1.77 (s, 6 H, CCH₃), 2.40, 2.52 (s \times 2, 6 H, NCH₃), 6.92 (d, 2 H, m-C₆H₃, $^3J_{HH} = 7.3$), 7.09 (t, 1 H, p-C₆H₃, $^3J_{HH} = 7.6$), 7.38–7.55 (m,

30 H, C₆H₅) ppm. $^{13}C\{^1H\}$: 236.3 (t, CS, $^2J_{CP} = 8.9$), 203.5 (t, CO, $^2J_{CP} = 12.5$), 158.5 (t, CN, J_{CP} not resolved), 135.4–126.5 (C₆H₅ + C₆H₃), 47.7, 46.2 (NCH₃), 17.87 (CCH₃) ppm. $^{31}P\{^1H\}$: 34.7 ppm. FAB-MS *m/z* (% abundance): 873 (79) [M]⁺, 611 (73) [M - PPh₃]⁺, 583 (100) [M - CO - PPh₃]⁺, 452 (35) [M - CO - isonitrile - PPh₃]⁺, 363 (13) [RuPPh₃]⁺. The corresponding hexafluorophosphate salt 7·PF₆ was prepared by anion metathesis of 7·Cl with NH₄[PF₆] in a mixture of dichloromethane, ethanol, and water and recrystallized from a mixture of chloroform and ethanol. Anal. Found: C, 53.9; H, 4.0; N, 2.5. C₄₉H₄₅F₆N₂OP₃RuS·0.75CHCl₃ requires: C, 54.0; H, 4.2; N, 2.5.

Preparation of [Rh(η^2 -SCNMe₂)Cl₂(PPh₃)₂] (8). (a) [RhCl-(PPh₃)₃] (1.00 g, 1.08 mmol) and Me₂NC(S)Cl (0.27 g, 2.19 mmol) were dried under vacuum and dissolved in degassed dichloromethane (30 mL), and the mixture was stirred for 2 h. On reduction of solvent volume (rotary evaporator) after addition of ethanol (30 mL), red crystals of the product formed. These were washed with ethanol (20 mL) and petroleum ether (20 mL), and dried in vacuo. Yield: 0.75 g (88%). (b) A suspension of [Rh(cod)(PPh₃)₂]PF₆ (0.50 g, 0.57 mmol) and Me₂-NC(S)Cl (0.14 g, 1.14 mmol) in tetrahydrofuran (15 mL) was stirred for 10 h under nitrogen. The red precipitate was filtered, washed with petroleum ether (25 mL), and dried. A further crop of product was obtained by addition of petroleum ether (50 mL) to the filtrate. Combined yield: 0.28 g (63%). IR CH₂Cl₂: 1607 ν_{NC} cm⁻¹. Nujol: 1608 ν_{NC} , 1311, 1223, 920 ν_{CS} , 826, 328, 300, 273 $\nu_{RhCl/\nu_{RHS}}$ cm⁻¹. NMR (CDCl₃, 25 °C) 1H : 2.16, 2.37 (s \times 2, 6 H, CH₃), 7.20–8.10 (m, 30 H, C₆H₅) ppm. $^{31}P\{^1H\}$: 18.6 ($J_{RHP} = 95.0$ Hz) ppm. FAB-MS *m/z* (% abundance): 750 (65) [M]⁺, 715 (4) [M - Cl]⁺, 488 (81) [M - PPh₃]⁺, 453 (20) [M - Cl - PPh₃]⁺, 409 (3) [M - Cl - NMe₂ - PPh₃]⁺. Anal. Found: C, 58.2; H, 4.4; N, 1.7. C₃₉H₃₆Cl₂NP₂RhS·0.25CH₂Cl₂ requires: C, 58.4; H, 4.6; N, 1.7 (CH₂Cl₂ by 1H NMR integration).

Preparation of [RhCl₂{ κ^2 -C(NMe₂)SC(=S)}(PPh₃)₂] (9). [RhCl(CS)(PPh₃)₂] (0.50 g, 0.71 mmol) and Me₂NC(S)Cl (0.17 g, 1.38 mmol) were dried under vacuum, and dry, degassed tetrahydrofuran (30 mL) was added under nitrogen. The resulting orange suspension was heated under reflux for 24 h to give a yellow-orange solid, which was filtered off (the filtrate was found to contain unreacted starting material) and then dissolved in dichloromethane (250 mL) and passed through diatomaceous earth to remove insoluble impurities. Pale orange crystals precipitated on reduction in solvent volume of this dichloromethane solution. These were isolated by filtration and washed with petroleum ether (30 mL) and dried. Yield: 0.35 g (60%). IR CH₂Cl₂: 1605 ν_{NC} cm⁻¹. Nujol: 1586 ν_{NC} , 1315, 1267, 1231, 1221, 1109, 973, 879, 855 cm⁻¹. NMR (CDCl₃, 25 °C) 1H : 2.33, 2.43 (s \times 2, 6 H, CH₃), 7.20–8.15 (m, 30 H, C₆H₅) ppm. Poor solubility precluded the successful acquisition of $^{13}C\{^1H\}$ or $^{31}P\{^1H\}$ NMR data. FAB-MS *m/z* (% abundance): 793 (29) [M - Cl]⁺, 750 (9) [M - Cl - {C(=S)}]⁺, 718 (3) [M - Cl - {C(=S)S}]⁺, 671 (13) [M - Cl - {C(=S)S} - NMe₂]⁺, 663 (10) [M - Cl - {C(=S)SC(NMe₂)}]⁺, 627 (15) [M - 2Cl - {C(=S)SC(NMe₂)}]⁺, 532 (26) [M - Cl - PPh₃]⁺, 497 (18) [M - 2Cl - PPh₃]⁺, 488 (22) [M - Cl - {C(=S)} - PPh₃]⁺, 456 (4) [M - Cl - {C(=S)S} - PPh₃]⁺, 453 (11) [M - 2Cl - {C(=S)} - PPh₃]⁺, 414 (24) [M - Cl - {C(=S)S} - NMe₂ - PPh₃]⁺, 400 (4) [M - Cl - {C(=S)SC(NMe₂)} - PPh₃]⁺, 377 (4) [M - 2Cl - {C(=S)S} - NMe₂ - PPh₃]⁺, 364 (5) [M - Cl₂ - {C(=S)SC(NMe₂)} - PPh₂]⁺. Anal. Found: C, 56.5; H, 4.3; N, 1.6. C₄₀H₃₆Cl₂NP₂RhS₂ requires: C, 56.4; H, 4.3; N, 1.6.

Preparation of [Ir(η^2 -SCNMe₂)Cl(CO)(PPh₃)₂]Cl (10·Cl). [IrCl(CO)(PPh₃)₂] (0.50 g, 0.64 mmol) and Me₂NC(S)Cl (0.16 g, 1.30 mmol) were dried under vacuum, and then dry, degassed tetrahydrofuran (20 mL) was added under nitrogen. This suspension was heated under reflux for 1 h. After cooling, the colorless crystals that formed were filtered off and washed with petroleum ether (30 mL). Yield: 0.55 g (95%). IR CH₂-Cl₂: 2042 ν_{CO} , 1623 ν_{NC} cm⁻¹. Nujol: 2014 ν_{CO} , 1622 ν_{NC} , 1315,

1215, 919 ν_{CS} , 844, 292 ν_{IrCl} cm^{-1} . NMR (CDCl_3 , 25 °C) ^1H : 1.77, 2.64 (s \times 2, 6 H, CH_3), 7.20–7.65 (m, 30 H, C_6H_5) ppm. $^{31}\text{P}\{^1\text{H}\}$: –2.4 ppm. $^{13}\text{C}\{^1\text{H}\}$: 193.7 (t, SCN, $^2J_{\text{CP}} = 4.5$), 169.8 (t, CO, $^2J_{\text{CP}} = 7.2$), 133.7 (t v , o/m- C_6H_5 , $J_{\text{CP}} = 5.4$), 132.1 (p- C_6H_5), 128.8 (t v , o/m- C_6H_5 , $J_{\text{CP}} = 5.4$), 126.0 (t v , i- C_6H_5 , $J_{\text{CP}} = 30.4$), 48.9, 46.2 (s \times 2, CH_3) ppm. FAB-MS m/z (% abundance): 868 (100) $[\text{M}]^+$, 840 (8) $[\text{M} - \text{CO}]^+$, 578 (26) $[\text{M} - \text{CO} - \text{PPh}_3]^+$, 542 (20) $[\text{M} - \text{Cl} - \text{CO} - \text{PPh}_3]^+$, 497 (2) $[\text{M} - \text{Cl} - \text{CO} - \text{NMe}_2 - \text{PPh}_3]^+$. Anal. Found: C, 50.0; H, 4.2; N, 1.5. $\text{C}_{41}\text{H}_{36}\text{Cl}_3\text{IrNOP}_2\text{S} \cdot 0.5\text{CH}_2\text{Cl}_2$ requires: C, 50.1; H, 4.0; N, 1.4.

Preparation of $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}_2(\text{PPh}_3)_2]$ (11). (a) $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ (0.22 g, 0.28 mmol) and $\text{Me}_2\text{NC}(\text{S})\text{Cl}$ (0.07 g, 0.57 mmol) were dried under vacuum, and dry, degassed dichloromethane (20 mL) was introduced under nitrogen. The reaction was stirred for 2 h, during which time the solution color changed to orange. The solvent volume was reduced to ca. 2 mL and the mixture placed on a silica column. The column was eluted with a dichloromethane/tetrahydrofuran (95:5) solvent mixture to give the desired product as the first bright red fraction. Crystallization was achieved from a dichloromethane/ethanol mixture to provide red crystals, which were washed with ethanol (10 mL) and petroleum ether (10 mL) and dried. Yield: 0.17 g (69%). (b) $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ (10-Cl) (0.15 g, 0.17 mmol) was dissolved in dichloromethane (20 mL) and then treated with HNMe_2 (1.0 mL, 2.0 mmol, 2 M solution in thf, Aldrich). The reaction was stirred for 40 h, during which the solution color became red. Ethanol (20 mL) was added and the solvent volume reduced by rotary evaporation until crystallization had occurred. The red product was washed with ethanol (10 mL) and petroleum ether (10 mL) and dried. Yield: 0.10 g (66%). (c) $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ (10-Cl) (0.050 g, 0.06 mmol) was dissolved in chloroform (2 mL) and then left in bright sunlight for 5 days. After this period deep red crystals had formed. These were isolated and washed with ethanol (5 mL) and petroleum ether (5 mL) and dried. Yield: 0.03 g (62%). IR $\text{CH}_2\text{-Cl}_2$: 1607 ν_{NC} cm^{-1} . Nujol: 1603 ν_{NC} , 1312, 1226, 916 ν_{CS} , 837 cm^{-1} . NMR (CDCl_3 , 25 °C) ^1H : 2.17, 2.20 (s \times 2, 6 H, CH_3), 7.20–8.10 (m, 30 H, C_6H_5) ppm. $^{31}\text{P}\{^1\text{H}\}$: –11.9 ppm. FAB-MS m/z (% abundance): 875 (36) $[\text{M}]^+$, 840 (100) $[\text{M} - \text{Cl}]^+$, 787 (2) $[\text{M} - \text{SCNMe}_2]^+$, 752 (1) $[\text{M} - \text{Cl} - \text{SCNMe}_2]^+$, 615 (4) $[\text{M} - \text{PPh}_3]^+$, 578 (17) $[\text{M} - \text{Cl} - \text{PPh}_3]^+$, 542 (25) $[\text{M} - 2\text{Cl} - \text{PPh}_3]^+$, 497 (5) $[\text{M} - 2\text{Cl} - \text{PPh}_3 - \text{NMe}_2]^+$. Anal. Found: C, 52.8; H, 4.2; N, 1.6. $\text{C}_{39}\text{H}_{36}\text{Cl}_2\text{IrNP}_2\text{S}$ requires: C, 53.5; H, 4.1; N, 1.6. Crystals of a bis(dichloromethane) solvate suitable for crystallographic analysis were grown by layering ethanol on a dichloromethane solution of the complex. *Crystal data for 11-(CH₂Cl₂)₂*: $\text{C}_{41}\text{H}_{40}\text{Cl}_6\text{IrNP}_2\text{S}$, $M_w = 1045.64$, triclinic, $P\bar{1}$ (#2), $a = 12.5073(18)$ Å, $b = 12.9507(16)$ Å, $c = 13.3127(11)$ Å, $\alpha = 85.265(7)^\circ$, $\beta = 87.535(12)^\circ$, $\gamma = 88.242(12)^\circ$, $V = 2146.2(4)$ Å³, $Z = 2$, $\mu(\text{Mo K}\alpha) = 3.638$ mm⁻¹, $D_{\text{calc}} = 1.618$ Mg m⁻³, $T = 293(2)$ K, yellow needles, 7546 independent measured reflections. $R_1 = 0.0456$, $wR_2 = 0.0980$, 5862 independent absorption-corrected reflections [$I > 2\sigma(I)$, $2\theta \leq 50^\circ$] and 453 parameters, CCDC 275852.

Preparation of $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CS})(\text{PPh}_3)_2]\text{Cl}$ (12-Cl). $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ (0.30 g, 0.38 mmol) and $\text{Me}_2\text{NC}(\text{S})\text{Cl}$ (0.05 g, 0.41 mmol) were dried under vacuum, and dry, degassed tetrahydrofuran (20 mL) was added under nitrogen. This suspension was heated under reflux anaerobically for 3 h, leading to a suspension. The product was filtered off, washed with petroleum ether (30 mL), and dried. Yield: 0.31 g (90%). The salt could be recrystallized from a mixture of dichloromethane and ethanol as a dichloromethane hemisolvate. IR $\text{CH}_2\text{-Cl}_2$: 1615 ν_{NC} cm^{-1} . Nujol: 1616 ν_{NC} , 1349 ν_{CS} , 1217, 921 ν_{CS} , 844 cm^{-1} . NMR (25 °C) ^1H (CDCl_3): 2.57, 2.77 (s \times 2, 6 H, CH_3), 7.40–7.85 (m, 30 H, C_6H_5) ppm. $^{13}\text{C}\{^1\text{H}\}$ (1:2 $\text{CDCl}_3/\text{CH}_2\text{-Cl}_2$): 254.5 (t, CS, $^2J_{\text{CP}} = 8.1$), 195.2 (t, SCN, $^2J_{\text{CP}} = 3.6$), 134.2 (t v , o/m- C_6H_5 , J_{CP} not resolved), 132.2 (s, p- C_6H_5), 128.8 (t v , o/m- C_6H_5 , J_{CP} not resolved), 126.3 (t v , i- C_6H_5 , $J_{\text{CP}} = 29.5$ Hz), 48.6, 45.3 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$: –0.7 ppm. FAB-MS m/z (% abundance): 884 (100) $[\text{M}]^+$, 622 (47) $[\text{M} - \text{PPh}_3]^+$, 587 (10) $[\text{M} - \text{Cl} - \text{PPh}_3]^+$, 542 (4) $[\text{M} - \text{Cl} - \text{CS} - \text{PPh}_3]^+$, 497 (10) $[\text{M} - \text{Cl} - \text{SCNMe}_2 - \text{CS} - \text{PPh}_3]^+$, 360 (4) $[\text{M} - (\text{PPh}_3)_2]^+$. A sample for microanalysis was crystallized from a mixture of dichloromethane and ethanol. Anal. Found: C, 50.8; H, 4.5; N, 1.4. $\text{C}_{40}\text{H}_{36}\text{Cl}_2\text{IrNP}_2\text{S}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ requires: C, 50.6; H, 3.9; N, 1.5. Crystals of **12-Cl(CHCl₃)₆** suitable for diffraction were grown by slow evaporation of a chloroform solution of the salt. *Crystal data for 12-Cl(CHCl₃)₆*: $\text{C}_{46}\text{H}_{42}\text{Cl}_{12}\text{IrNP}_2\text{S}_2$, $M_w = 1636.07$, triclinic, $P\bar{1}$ (#2), $a = 9.513(2)$ Å, $b = 14.790(2)$ Å, $c = 24.540(2)$ Å, $\alpha = 73.757(11)^\circ$, $\beta = 87.499(12)^\circ$, $\gamma = 87.346(18)^\circ$, $V = 3309.7(10)$ Å³, $Z = 2$, $\mu(\text{Mo K}\alpha) = 2.968$ mm⁻¹, $D_{\text{calc}} = 1.642$ Mg m⁻³, $T = 293(2)$ K, clear platy needles, 6326 independent measured reflections, $R_1 = 0.0504$, $wR_2 = 0.1314$, 5306 independent absorption-corrected reflections [$I > 2\sigma(I)$, $2\theta \leq 45^\circ$], 616 parameters, CCDC 275853.

Preparation of $[\text{Ir}(\eta^2\text{-SCNMe}_2)\{\eta^1\text{-C(=O)H}\}\text{Cl}(\text{PPh}_3)_2]$ (13). $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ (10: 0.20 g, 0.22 mmol) was dissolved in dichloromethane (10 mL) and ethanol added (20 mL). A filtered solution of NaBH_4 (0.10 g, 2.63 mmol) in ethanol (15 mL) was added and the reaction stirred for 30 min. The colorless precipitate was filtered, washed with ethanol (20 mL) and petroleum ether (30 mL), and dried. Yield: 0.19 g (99%). The complex could be recrystallized from a mixture of dichloromethane and ethanol as a dichloromethane hemisolvate. IR $\text{CH}_2\text{-Cl}_2$: 2720, 2592 ν_{CH} , 1618 ν_{CO} , 1568 ν_{CN} cm^{-1} . Nujol: 2700, 2670, 2572 ν_{CH} , 1620 ν_{CO} , 1562, 1556 ν_{CN} , 1342, 1317, 1236, 930 ν_{CS} cm^{-1} . NMR (CDCl_3 , 25 °C) ^1H : 2.11, 2.38 (s \times 2, 6 H, CH_3), 7.73, 7.28 (m \times 2, 30 H, C_6H_5), 14.67 (t, 1 H, HCO, $^3J_{\text{HP}} = 6.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$: 2.4 ppm. $^{13}\text{C}\{^1\text{H}$ coupled): 215.2 (dt, HCO, $^1J_{\text{CH}} = 164.2$, $^2J_{\text{CP}} = 5.4$), 205.3 (s br, CS, $^2J_{\text{CP}}$ not resolved), 135.0 (dt v , o/m- C_6H_5 , J_{CP} not resolved, $^1J_{\text{CH}} = 162.4$), 131.4 (s, p- C_6H_5), 127.7 (dt v , o/m- C_6H_5 , J_{CP} not resolved, $^1J_{\text{CH}} = 161.3$), 130.6 (tt v , i- C_6H_5 , $J_{\text{PC}} = 23.2$, $^2J_{\text{CH}} = 7.2$), 43.4, 42.9 (q \times 2, CH_3 , $^1J_{\text{CH}} = 139.2$ Hz) ppm. FAB-MS m/z (% abundance): 868 (100) $[\text{M}]^+$, 834 (13) $[\text{M} - \text{Cl}]^+$, 805 (7) $[\text{M} - \text{Cl} - \text{HCO}]^+$, 752 (3) $[\text{M} - \text{HCO} - \text{SCNMe}_2]^+$, 715 (3) $[\text{M} - \text{Cl} - \text{HCO} - \text{SCNMe}_2]^+$, 605 (3) $[\text{M} - \text{PPh}_3]^+$, 578 (41) $[\text{M} - \text{HCO} - \text{PPh}_3]^+$, 542 (33) $[\text{M} - \text{Cl} - \text{HCO} - \text{PPh}_3]^+$. Anal. Found: C, 52.5; H, 3.6; N, 1.3. $\text{C}_{40}\text{H}_{37}\text{ClIrNOP}_2\text{S} \cdot 0.5\text{CH}_2\text{Cl}_2$ requires: C, 52.4; H, 4.1; N, 1.5 (CH_2Cl_2 by ^1H NMR integration).

Preparation of $[\text{Ir}(\eta^2\text{-SCNMe}_2)\{\eta^1\text{-C(=O)OEt}\}\text{Cl}(\text{PPh}_3)_2]$ (14). $[\text{Ir}(\eta^2\text{-SCNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{Cl}$ (10: 0.20 g, 0.22 mmol) was added to an ethanolic solution of NaOEt [prepared by dissolving sodium (0.2 g) in ethanol (20 mL)], giving rise to a rapid reaction involving a brief color change to yellow as the starting material reacted in solution before precipitating as a colorless product. After stirring for 30 min to ensure complete reaction, the crystals were filtered off, washed with ethanol, and recrystallized from dichloromethane and ethanol. The colorless product was washed with petroleum ether (20 mL) and hexane (10 mL) and dried. Yield: 0.18 g (89%). IR $\text{CH}_2\text{-Cl}_2$: 1605 ν_{CO} , 1573 ν_{NC} cm^{-1} . Nujol: 1618 ν_{CO} , 1578, 1572 ν_{NC} , 1315, 1231, 1169, 1041, 914 ν_{CS} , 865 cm^{-1} . NMR (CDCl_3 , 25 °C) ^1H : 0.66 (t, 3 H, CCH_3 , $^3J_{\text{HH}} = 7.3$), 2.14, 2.20 (s \times 2, 6 H, NCH_3), 3.57 (q, 2 H, OCH_2 , $^2J_{\text{HH}} = 7.3$ Hz), 7.20–8.10 (m, 30 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$: 202.0 (t, SCN, J_{CP} not resolved), 168.3 (t, CO_2 , $^2J_{\text{CP}} = 6.3$), 135.1 (t v , o/m- C_6H_5 , J_{CP} not resolved), 132.3 (t v , i- C_6H_5 , $J_{\text{CP}} = 26.8$), 129.5 (s, p- C_6H_5), 127.3 (t v , o/m- C_6H_5 , J_{CP} not resolved), 59.8 (OCH_2), 44.8, 42.2 (NCH_3), 14.1 (CCH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$: –6.5 ppm. FAB-MS m/z (% abundance): 913 (9) $[\text{M}]^+$, 878 (8) $[\text{M} - \text{Cl}]^+$, 868 (32) $[\text{M} - \text{OEt}]^+$, 840 (11) $[\text{M} - \text{CO}_2\text{Et}]^+$, 806 (3) $[\text{M} - \text{Cl} - \text{CO}_2\text{Et}]^+$, 745 (12) $[\text{M} - \text{Cl} - \text{OEt} - \text{SCNMe}_2]^+$, 715 (2) $[\text{Ir}(\text{PPh}_3)_2]^+$, 651 (2) $[\text{M} - \text{PPh}_3]^+$, 606 (5) $[\text{M} - \text{OEt} - \text{PPh}_3]^+$, 578 (25) $[\text{M} - \text{CO}_2\text{Et} - \text{PPh}_3]^+$, 542 (26) $[\text{M} - \text{Cl} - \text{CO}_2\text{Et} - \text{PPh}_3]^+$, 497 (6) $[\text{IrCS}(\text{PPh}_3)]^+$. Anal. Found: C, 54.5; H, 4.4; N, 1.5. $\text{C}_{42}\text{H}_{41}\text{ClIrNO}_2\text{P}_2\text{S} \cdot 0.25\text{CH}_2\text{-Cl}_2$ requires: C, 54.3; H, 4.5; N, 1.5.

Acknowledgment. We are grateful to the EPSRC (UK) for funding and contributions toward diffraction

equipment. One of us (J.D.E.T.W.-E.) gratefully acknowledges the Ramsay Memorial Trust for provision of a Fellowship. We would like to thank Johnson Matthey Ltd. for the generous loan of ruthenium salts.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations

of **2**·**PF**₆ (CCDC 275850), **3**·**CHCl**₃ (CCDC 275851), **11**·**(CH**₂**Cl**₂)₂ (CCDC 275852), and **12**·**(CHCl**₃)₆ (CCDC 275853); Table S1 collating structural data for metallathiirenes of ruthenium, rhodium, and iridium. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050514C