Mixed-Donor Ligands: Pyrrolecarbaldehyde and Pyrrolecarbothioaldehyde σ-Organyl Complexes of Ruthenium(II) and Osmium(II)

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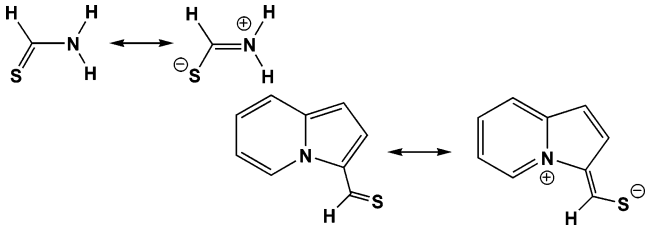
Vilsmair salts have been used to prepare a series of thioaldehyde molecules conjugated with a pyrrole ring (pyrrole substituents: H, Me, Et). The reaction of 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde (HL_4) with $[RuHCl(CO)(PPh_3)_3]$ or $[RuHCl(CO)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-benzothiadiazole) in the presence of NaOMe leads to the complex $[RuH(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$, in which the carbothioaldehyde ligand acts as a bidentate, three-electron donor. The same approach yields the aryl, alkenyl, and alkynyl complexes $[RuR(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$ (R = C_6H_5, $CH{=}CH_2$, CH=CHPh, $CH{=}CHC_6H_4Me$-4, CH=CH^{t}Bu, $CH{=}CHCPh_2OH$, $CH{=}CH(HO)C_6H_{10}$, C(C≡CPh)=CHPh, C≡CPh). The compound $[Ru(CH{=}CHCPh_2OH)(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$ can be dehydrated by reaction with HBF_4 to yield the vinylcarbene species $[Ru(=CHCH{=}CPh_2)(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]BF_4$. The complexes $[RuR(\kappa^2\text{-}L_6)(CO)(PPh_3)_2]$ (R = H, $CH{=}CH_2$, $CH{=}CHC_6H_4Me$-4, C(C≡CPh)=CHPh) were prepared from pyrrole-2-carboxaldehyde (HL_6), the oxygen analogue of the carbothioaldehyde ligands. Additionally, the osmium ethenyl compounds $[Os(CH{=}CH_2)(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$ and $[Os(CH{=}CH_2)(\kappa^2\text{-}L_6)(CO)(PPh_3)_2]$ were synthesized from $[Os(CH{=}CH_2)Cl(CO)(BTD)(PPh_3)_2]$ with either HL_4 or HL_6 in the presence of NaOMe. The crystal structures of the principal ligand and three representative complexes are reported.

Introduction

Thioaldehydes[1] are relatively rare in organic chemistry compared to their ubiquitous oxygen analogues. The paucity of examples is often attributed to the reluctance of sulfur to participate in multiple-bond formation and, as a result, oligomers and polymers are often formed. The reactivity of thiocarbonyl compounds is greatly influenced by the nature of the groups attached to the thiocarbonyl carbon atom. The more effective these substituents are in polarizing the C=S bond to the C^+-S^- form and in delocalizing the resultant positive charge, the greater the resistance the thiocarbonyl shows toward oligomerization and polymerization. This can be achieved when a heteroatom with the ability to donate a lone pair is bonded directly to (or in conjugation with) the thiocarbonyl carbon (Chart 1).

Chart 1. Polarization of C=S Bond and Delocalization of Charge through Heteroatom Interaction



However, this is not the only method of curbing the reactivity of thioaldehydes. Okazaki and co-workers reported that steric effects could also be used to hinder oligomerization and polymerization reactions, as demonstrated by the compound 2,4,6-(^{t}Bu)$_3$C$_6$H$_2$CSH.[2] The first carbothioaldehyde to be isolated was reported by Woodward and co-workers in 1950 as an important intermediate in the synthesis of chlorophyll (Scheme 1).[3] Although the only physical measurement reported for this compound was a melting point, the donor possibilities suggested by a combination of thioaldehyde ligand and pyrrole ring provided us with the inspiration to investigate this class of compounds further.

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(1) For reviews of synthetic routes to thioaldehydes and their use in organic synthesis, see: McGregor, W. M.; Sherrington, D. C. *Chem. Soc. Rev.* **1993**, *22*, 199. Kirby, G. W. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *74*, 17.

(2) Okazaki, R.; Ishii, A.; Fakuda, N.; Oyama, H.; Inamoto, N. *Chem. Commun.* **1982**, 1187.

(3) Woodward, R. B.; Ayer, W. A.; Beaton, J. M.; Bickelhaupt, F.; Bonnett, R.; Buchschacher, P.; Closs, G. L.; Dutler, H.; Hannah, J.; Hauck, F. F.; Ito, S.; Langemann, A.; Le Goff, E.; Leimgruber, W.; Lwowski, W.; Sauer, J.; Valenta, Z.; Volz, H. *J. Am. Chem. Soc.* **1960**, *82*, 3800.

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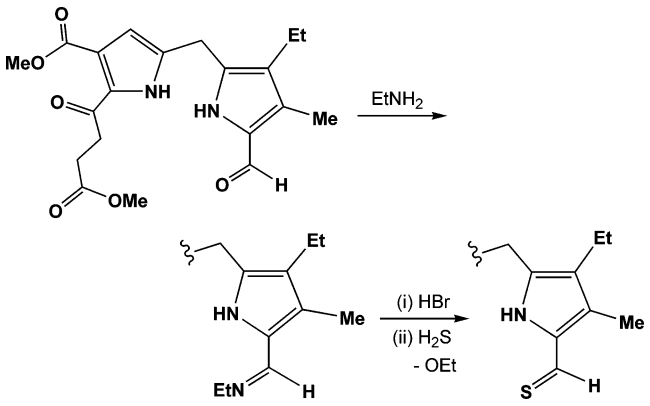
Scheme 1. Pyrrolecarbothioaldehyde Isolated en Route to Chlorophyll



Since the first report of a coordinated thioformaldehyde ligand by Roper,[4] a number of thioaldehyde complexes have been prepared.[5] These consist of complexes such as those reported by Roper, in which the thioaldehyde moiety is coordinated through both carbon and sulfur in an η^2 fashion,[5−8] and examples where the thioaldehyde is bonded solely through the sulfur lone pair.[5,9−12] A number of routes to this latter type of complex have been discovered. These include reaction of an anionic complex containing an −SH ligand with (usually aromatic) aldehydes[9] and aldimines[11] and treatment of Fischer carbene complexes with elemental sulfur. The selenium and tellurium analogues are also accessible by the carbene route.[10]

Coordinatively unsaturated ruthenium and osmium complexes containing σ-organyl ligands have been known since the late 1970s and have been shown to display a rich reactivity based on the vacant coordination site at the metal center.[13] In 1986, Werner and Esteruelas[14] reported the preparation of the 16-electron hydride complex $[RuHCl(CO)(P^iPr_3)_2]$. The subsequent discovery by the same authors that this compound readily hydroruthenates both primary and secondary alkynes[15] opened up an extensive chemistry starting from the coordinatively unsaturated products $[Ru(CR{=}CHR')Cl(CO)(P^iPr_3)_2]$. The parallel discovery by Santos[16] that the related triphenylphosphine compound $[RuHCl(CO)(PPh_3)_3]$ also hydrometalates alkynes provided an alternative entry point to ruthenium alkenyl chemistry via the series $[Ru(CR{=}CHR')Cl(CO)(PPh_3)_2]$. Evidence for the importance of this area is provided by the continued interest over the last 15 years.[17−20] More recently, the hydrometalation approach has been extended to include the preparation of phosphaalkenyl complexes which display a rich and varied chemistry of their own.[21]

Previous works by members of this group have centered on the reactivity of alkenyl complexes toward bi- and tridentate polypyrazolylborate[22] and sulfur macrocycle ([9]aneS_3)[23] donors. The reports involving bidentate ligands have concentrated mainly on sym-

(4) Collins, T. J.; Roper, W. R. *Chem. Commun.* **1977**, 901.

(5) Fischer, H.; Strumpf, R.; Roth, G. *Adv. Organomet. Chem.* **1999**, *43*, 125. Schenk, W. A. *J. Organomet. Chem.* **2002**, *661*, 129.

(6) (a) Hoffman, L.; Werner, H. *Chem. Ber.* **1985**, *118*, 4229. (b) Werner, H.; Hoffmann, L.; Wolf, J.; Müller, G. *J. Organomet. Chem.* **1985**, *280*, C55. (c) Buchwald, S. L.; Nielsin, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590. (d) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056. (e) Buhro, W. E.; Etter, M. C.; Georgion, S.; Gladysz, J. A.; McCormick, F. B. *Organometallics* **1987**, *6*, 1150. (f) McCormick, F. B. *J. Am. Chem. Soc.* **1984**, *3*, 1924. (g) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 310. (h) Schenk, W. A.; Vedder, B.; Klüglein, M.; Moigno, D.; Kiefer, W. *Dalton* **2002**, 3123.

(7) Burzlaff, N.; Schenk, W. A. *Eur. J. Inorg. Chem.* **1999**, 1435.

(8) Schenk, W. A.; Vedder, B.; Eichhorn, C. *Inorg. Chim. Acta* **2004**, *357*, 1886.

(9) Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604. Gingerich, R. G. W.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *132*, 377.

(10) Fischer, H.; Zeuner, S.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 726. Fischer, H.; Zeuner, S. *Z. Naturforsch.* **1985**, *40b*, 954.

(11) Muraoka, M.; Yamamoto, T.; Ajimi, S.; Yamaguchi, H.; Koinuma, T. *J. Chem. Soc., Perkin Trans.* **1994**, 667.

(12) Kuhnert, N.; Burzlaff, N.; Dombrowski, E.; Schenk, W. A. *Z. Naturforsch.* **2002**, *57b*, 259.

(13) For a review of the hydrometalation of alkynes and σ-alkenyl complexes or ruthenium, see: Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 7.

(14) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *221*, 303.

(15) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(16) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *309*, 169.

(17) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *Eur. J. Inorg. Chem.* **2004**, 469. Jung, S.; Brandt, C. D.; Wolf, J.; Werner, H. *Dalton* **2004**, 375. Werner, H.; Jung, S.; Gonzalez-Herrero, P.; Ilg, K.; Wolf, J. *Eur. J. Inorg. Chem.* **2001**, 1957. Jung, S.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 2121. Werner, H.; Stüer, W.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **2002**, 1076. Werner, H.; Stark, A.; Steinert, P.; Grunwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49.

(18) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294. Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. *Organometallics* **2000**, *19*, 5098. Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2000**, *19*, 5454. Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176. Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373. Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E. *Organometallics* **1998**, *17*, 3567. Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919. Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748. Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E. *J. Am. Chem. Soc.* **1996**, *118*, 89. Bohanna, C.; Esteruelas, M. A.; Herrero, J.; López, A. M.; Oro, L. A. *J. Organomet. Chem.* **1995**, *498*, 199. Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E. *Organometallics* **1995**, *14*, 4825. Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685.

(19) (a) Gómez-Lor, B.; Santos, A.; Ruiz, M.; Echavarren, A. M. *Eur. J. Inorg. Chem.* **2001**, 2305. (b) Castaño, A. M.; Echavarren, A. M.; López, J.; Santos, A. *J. Organomet. Chem.* **1989**, *379*, 171. (c) Montoya, J.; Santos, A.; Echavarren, A. M.; Ros, J. *J. Organomet. Chem.* **1990**, *390*, C57. (d) Loumrhari, H.; Ros, J.; Torres, M. R.; Santos, A.; Echavarren, A. M. *J. Organomet. Chem.* **1991**, *411*, 255. (e) Montoya, J.; Santos, A.; López, J.; Echavarren, A. M.; Ros, J.; Romero, A. *J. Organomet. Chem.* **1992**, *426*, 383. (f) López, J.; Romero, A.; Santos, A.; Vegas, A.; Echavarren, A. M.; Noheda, P. *J. Organomet. Chem.* **1989**, *373*, 249.

(20) Pedersen, A.; Tilset, M.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 875. Marchenko, A. V.; Gérard, H.; Eisenstein, O.; Caulton, K. G.; *New. J. Chem.* **2001**, *25*, 1244. Marchenko, A. V.; Gérard, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 1382.

(21) Bedford, R. B.; Hill, A. F.; Jones, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 547. Bedford, R. B.; Hibbs, D. E.; Hill, A. F.; Hursthouse, M. B.; Malik, K. M. A.; Jones, C. *Chem. Commun.* **1996**, 1895. Bedford, R. B.; Hill, A. F.; Jones, C.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1997**, 139. Bedford, R. B.; Hill, A. F.; Jones, C.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1997**, 179. Hill, A. F.; Jones, C.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T.; *Chem. Commun.* **1998**, 367. Hill, A. F.; Jones, C.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1998**, 1419. Bedford, R. B.; Hill, A. F.; Jones, C.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 4744. Hill, A. F.; Jones, C.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 451.

(22) (a) Cartwright, J.; Hill, A. F. *J. Organomet. Chem.* **1992**, *429*, 229. (b) Alcock, N. W.; Hill, A. F.; Melling, R. P. *Organometallics* **1991**, *10*, 3898. (c) Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 4249.

metrical chalcogen donors such as carboxylates,[24] dithiocarbamates,[25] and dithiophosphinates,[26] but have not been extended to systems in which two different donor atoms are involved in chelation. Our current research program seeks to address this situation by focusing on the coordination properties of nitrogen−sulfur and nitrogen−oxygen mixed-donor chelates with ruthenium and osmium alkenyl complexes and how these ligands effect their reactivity (e.g., hemilabile behavior).

This report details the synthesis of a family of unusual pyrrole carbothioaldehyde molecules and their use as three-electron bidentate nitrogen−sulfur chelates for complexes bearing hydride and σ-organyl ligands.

Experimental Section

Apart from where stated, all manipulations were carried out under aerobic conditions using commercially available solvents and reagents as received. Infrared spectra were obtained on a Shimadzu FTIR 8700 spectrometer using KBr plates unless stated otherwise. Infrared spectroscopic features due to the triphenylphosphine ligands are not reported. NMR spectroscopy was carried out using Bruker AMX-300 (^{1}H, 299.9 MHz; ^{31}P, 121.4 MHz; ^{13}C, 75.4 MHz) and Bruker DRX-500 (^{1}H, 501.1 MHz; ^{13}C, 125.77 MHz) spectrometers. All spectra were recorded at 25 °C unless otherwise indicated. FAB-MS spectra (nitrobenzyl alcohol matrices) were measured using a VG 70-SB magnetic sector mass spectrometer. Elemental analyses were performed at the University of St. Andrews and University College London. Crystal solvates were confirmed by integration of the dichloromethane resonance in the ^{1}H NMR spectra of the complexes. 2,1,3-Benzothiadiazole is abbreviated as BTD throughout. The compounds [RuHCl(CO)(PPh$_3$)$_3$],[27] [RuHCl(CO)(BTD)(PPh$_3$)$_2$],[28] [Ru(CH=CHPh)Cl(CO)(PPh$_3$)$_2$],[16] [Ru(CH=CHC$_6$H$_4$CH$_3$-4)Cl(CO)(BTD)(PPh$_3$)$_2$],[29] [Ru(CH=CH$_2$)Cl(CO)(PPh$_3$)$_2$],[23,30] [Ru(CH=CH^{t}Bu)Cl(CO)(PPh$_3$)$_2$],[30] [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh$_3$)$_2$],[31] [Ru(C≡CPh)Cl(CO)(BTD)(PPh$_3$)$_2$],[32] [Ru(CH=CHCPh$_2$OH)Cl(CO)(BTD)(PPh$_3$)$_2$],[29] [Ru{CH=CH(HO)C$_6$H$_{10}$}(BTD)(PPh$_3$)$_2$],[33] [Ru(C$_6$H$_5$)Cl(CO)(PPh$_3$)$_2$],[34] [OsHCl(CO)(BTD)(PPh$_3$)$_2$],[35] [Os(CH=CH$_2$)Cl(CO)(BTD)(PPh$_3$)$_2$],[35] 2-methylpyrrole,[36] 2,3-dimethylpyrrole,[37] 3,4-dimethylpyrrole,[38] and 1,2,3-trimethylpyrrole[39] were prepared according to published procedures. All other materials were purchased commercially and used as received. See Chart 3 for numbering of the ethenyl ligand.

Procedure for the Preparation of Pyrrolecarbothioaldehyde Ligands (HL_1−HL_4 and L_5). A solution of the pyrrole (10 mmol) in dimethylformamide (10 mL) was added dropwise over a period of 10 min to a stirred solution of phosphorus oxychloride (1 mL, 1.65 g, 10.76 mmol) in dimethylformamide (10 mL). The resulting solution was stirred at room temperature for 30 min and then poured into aqueous (2 M) sodium hydrogen sulfide (50 mL). The mixture was diluted with water (200 mL) and then extracted with diethyl ether (3 × 100 mL). The extracts were washed with water (6 × 100 mL), dried, and evaporated to dryness. The residue was dissolved in a minimum volume of benzene and chromatographed on alumina with benzene as eluant. The eluates were collected and the solvent removed. The products **HL_1**−**HL_4 and HL_5** were crystallized as described below for each compound.

5-Methylpyrrole-2-carbothioaldehyde (HL_1). Carbothioaldehyde **HL_1** was obtained as a cherry red solid (0.908 g, 73%) from 2-methylpyrrole (0.811 g). The product is unstable to air and moisture over extended storage periods. Samples were stored under nitrogen at −20 °C. ^{1}H NMR (CDCl$_3$, 33 °C): 2.31 (s, Me^5, 3H), 6.18 (d, H^4, 1H, J_{HH} = 3.8 Hz), 6.71 (d, H^3, 1H, J_{HH} = 3.8 Hz), 9.10 (s (br), NH, 1H), 10.41 (s, CSH, 1H) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 38 °C): 13.8 (s, Me^5), 113.4 (s, C^4), 122.6 (s, C^3), 143.3 (s, C^2), 143.5 (s, C^5), 198.4 (s, CSH) ppm. Anal. Calcd for C$_6$H$_7$NS: C, 57.6; H, 5.6; N, 11.2. Found: C, 57.5; H, 5.7; N, 10.9.

3,4-Dimethylpyrrole-2-carbothioaldehyde (HL_2). Reaction of 3,4-dimethylpyrrole (0.951 g) gave the carbothioaldehyde **HL_2** (0.932 g, 67%) as brown needles from cyclohexane. ^{1}H NMR (CDCl$_3$, 33 °C): 2.02 (s, Me^4, 3H), 2.19 (s, Me^3, 3H), 7.06 (s, H^5, 1H, J_{HH} = 3.0 Hz), 9.30 (s (br), NH, 1H), 10.62 (s, CSH, 1H) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 38 °C): 9.2 (s, Me^4), 9.6 (s, Me^3), 123.0 (s, C^4), 130.2 (s, C^3), 130.3 (s, C^2), 142.2 (s, C^5), 196.4 (s, CSH) ppm. Anal. Calcd for C$_7$H$_9$NS: C, 60.4; H, 6.5; N, 10.1. Found: C, 60.4; H, 6.7; N, 10.0.

4,5-Dimethylpyrrole-2-carbothioaldehyde (HL_3). Reaction of 2,3-dimethylpyrrole (0.951 g) gave carbothioaldehyde **HL_3** (0.914 g, 66%) as orange plates from cyclohexane. ^{1}H NMR (CDCl$_3$, 33 °C): 2.02 (s, Me^4, 3H), 2.20 (s, Me^5, 3H), 6.56 (s, H^3, 1H), 9.48 (s (br), NH, 1H), 10.27 (s, CSH, 1H) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 38 °C): 10.7 (s, Me^4), 12.1 (s, Me^5), 122.6 (s, C^4), 122.9 (s, C^3), 141.6 (s, C^2), 142.1 (s, C^5), 196.2 (s, CSH) ppm. Anal. Calcd for C$_7$H$_9$NS: C, 60.4; H, 6.5; N, 10.1. Found: C, 60.1; H, 6.6; N, 10.0.

3,5-Dimethyl-4-ethylpyrrole-2-carbothioaldehyde (HL_4). Reaction of 2,4-dimethyl-3-ethylpyrrole (1.232 g) gave carbothioaldehyde **HL_4** (1.122 g, 67%) as orange prisms from acetonitrile. ^{1}H NMR (CDCl$_3$, 25 °C, 500.1 MHz): 1.03 (t, CH$_2$C*H*$_3$, 3H, J_{HH} = 7.6 Hz), 2.15 (s, Me^3, 3H), 2.21 (s, Me^5, 3H), 2.35 (q, C*H*$_2$CH$_3$, 2H, J_{HH} = 7.6 Hz), 9.34 (s (br), NH, 1H), 10.23 (s, CSH, 1H) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C, 500.1 MHz): 9.2 (s, Me^3), 12.1 (s, Me^5), 14.6 (s, CH$_2$*C*H$_3$), 17.0 (s, *C*H$_2$CH$_3$), 127.6 (s, C^4), 131.0 (s, C^3), 141.2 (s, C^2), 142.2 (s, C^5), 190.6 (s, CSH) ppm. IR (KBr/Nujol): 1556, 1261, 1107, 893, 841 cm^{-1}. Anal. Calcd for C$_9$H$_{13}$NS: C, 64.6; H, 7.8; N, 8.4. Found: C, 64.7; H, 7.9; N, 8.3.

1,4,5-Trimethylpyrrole-2-carbothioaldehyde (L_5). Reaction of 1,2,3-trimethylpyrrole (1.092 g) gave the carbothioaldehyde **L_5** (0.477 g, 31%) as red prisms from hexane. ^{1}H NMR (CDCl$_3$, 33 °C): 2.01 (s, Me^4, 3H), 2.14 (s, Me^5, 3H), 3.90 (s, NMe, 3H), 6.74 (s, H^3, 1H), 10.46 (s, CSH, 1H) ppm. Anal. Calcd for C$_8$H$_{11}$NS: C, 62.7; H, 7.2; N, 9.1. Found: C, 62.4; H, 7.1; N, 9.1.

General Procedure for the Preparation of Pyrrolecarbothioaldehyde and Pyrrolecarboxaldehyde Com-

(23) Cannadine, J. C.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1996**, *15*, 5409.
(24) (a) Loumrhari, H.; Matas, L.; Ros, J.; Torres, M. R.; Perales, A. *J. Organomet. Chem.* **1991**, *403*, 373. (b) Torres, M. R.; Perales, A.; Loumrhari, H.; Ros, J. *J. Organomet. Chem.* **1990**, *384*, C61. (c) Loumrhari, H.; Ros, J.; Yáñez, R.; Torres, M. R. *J. Organomet. Chem.* **1991**, *408*, 233. (d) Torres, M. R.; Perales, A.; Loumrhari, H.; Ros, J. *J. Organomet. Chem.* **1990**, *385*, 379.
(25) Loumrhari, H.; Ros, J.; Torres, M. R. *Polyhedron* **1991**, *10*, 421. Bedford, R. B.; Cazin, C. S. J. *J. Organomet. Chem.* **2000**, *598*, 20.
(26) Hector, A. L.; Hill, A. F. *J. Organomet. Chem.* **1993**, *447*, C7.
(27) Laing, K. R.; Roper, W. R. *J. Chem. Soc. A* **1970**, 2149.
(28) Procedure modified substituting BTD for BSD from: Alcock, N. W.; Hill, A. F.; Roe, M. S. *J. Chem. Soc., Dalton Trans.* **1990**, 1737.
(29) Procedure modified substituting BTD for BSD from: Harris, M. C. J.; Hill, A. F. *Organometallics* **1991**, *10*, 3903.
(30) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1987**, *326*, 413.
(31) Hill, A. F.; Melling, R. P. *J. Organomet. Chem.* **1990**, *396*, C22. Hill, A. F.; Harris, M. C. J.; Melling, R. P. *Polyhedron* **1992**, *11*, 781.
(32) Bedford, R. B.; Hill, A. F.; Thompsett, A. R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 1059.
(33) Harris, M. C. J.; Hill, A. F. *J. Organomet. Chem.* **1992**, *438*, 209.
(34) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375.
(35) Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1998**, 3501.
(36) Silverstein, R. M.; Ryskiewicz, E. E.; Willard, C. *Org. Synth.* **1956**, *36*, 74. Cornforth, J. W.; Firth, M. E. *J. Chem. Soc.* **1958**, 1091.
(37) Roomi, M. W.; MacDonald, S. F. *Can. J. Chem.* **1970**, *48*, 1689.
(38) Hinman, R. L.; Theodoropulous, S. *J. Org. Chem.* **1963**, *28*, 3052.
(39) Potts, K. J.; Saxton, J. E. *Org. Synth.* **1960**, *40*, 68.

plexes. The ruthenium or osmium complex (typically 0.120 mmol) and **HL$_4$** or **HL$_6$** (0.132 mmol) was suspended in a mixture of dichloromethane (15 mL) and ethanol (10 mL) and treated with sodium methoxide (0.240 mmol) in ethanol (10 mL). The mixture was stirred for 1 h and the solvent volume concentrated under reduced pressure until precipitation of the product was complete. This was washed with water (5 mL), ethanol (10 mL), and hexane (10 mL). All products can be recrystallized from dichloromethane and ethanol.

[RuH(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (1). The product was brick red (61 mg, 71%), obtained from [RuHCl(CO)(PPh$_3$)$_3$] (100 mg) or, alternatively, in 83% yield (82 mg) from [RuHCl(CO)(BTD)-(PPh$_3$)$_2$] (100 mg). Yield: 82 mg (83%). IR (KBr/Nujol): 1919 (ν(CO)), 1556, 1259, 907, 858 cm^{-1}. IR (CH_2Cl_2): 1925 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6): 17.1 ppm. ^{1}H NMR (C_6D_6): −10.61 (t, RuH, 1H, J_{PH} = 19.9 Hz), 0.92 (t, CH_2CH_3, 3H, J_{HH} = 7.5 Hz), 1.62 (s, Me^3, 3H), 1.70 (s, Me^5, 3H), 2.01 (q, CH_2CH_3, 3H, J_{HH} = 7.5 Hz), 6.93−8.25 (m, C_6H_5 + CSH, 30H + 1H) ppm. FAB-MS (*m/z* (abundance, %)): 821 (32) [M]$^+$, 791 (3) [M − CO]$^+$, 654 (5) [M − L$_4$]$^+$, 558 (5) [M − PPh$_3$]$^+$, 530 (22) [M − CO − PPh$_3$]$^+$. Anal. Calcd for $C_{46}H_{43}NOP_2RuS$: C, 67.3; H, 5.3; N, 1.7. Found: C, 67.7; H, 5.3; N, 1.8.

[Ru(CH=CH$_2$)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (2). Pale brown microcrystals (50 mg, 53%) were obtained from [Ru(CH=CH$_2$)Cl-(CO)(PPh$_3$)$_2$] (80 mg). IR (KBr/Nujol): 1946 (ν(CO)), 1549, 1258, 1005, 907, 860 cm^{-1}. IR (CH_2Cl_2): 1946 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): 31.9 ppm. ^{1}H NMR ($CDCl_3$): 0.89 (t, CH_2CH_3, 3H, J_{HH} = 7.6 Hz), 1.63 (s, Me^3, 3H), 1.77 (s, Me^5, 3H), 2.05 (q, CH_2CH_3, 2H, J_{HH} = 7.6 Hz), 4.88 (ddt, Hβ, 1H, $J_{H\beta H\alpha}$ = 18.2, $J_{H\beta H\beta'}$ = 3.5 Hz, $J_{H\beta P}$ = 1.5 Hz), 5.64 (ddt, Hβ' 1H, $J_{H\beta' H\alpha}$ = 10.8, $J_{H\beta' H\beta}$ = 3.5 Hz, $J_{H\beta' P}$ = 2.0 Hz), 7.13−7.46 (m, C_6H_5 + CSH, 30H + 1H), 8.04 (ddt, Hα, 1H, $J_{H\alpha H\beta}$ = 18.2, $J_{H\alpha H\beta'}$ = 10.8 Hz, $J_{H\alpha P}$ = 2.9 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 846 (1) [M]$^+$, 819 (1) [M − alkenyl]$^+$, 584 (0.9) [M − PPh$_3$]$^+$, 556 (2) [M − alkenyl − PPh$_3$]$^+$, 528 (1) [M − alkenyl − CO − PPh$_3$]$^+$. Anal. Calcd for $C_{48}H_{45}NOP_2RuS\cdot 0.5CH_2Cl_2$: C, 65.5; H, 5.2; N, 1.6. Found: C, 65.2; H, 5.2%; N, 1.6.

[Ru(CH=CHPh)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (3). The pale orange product (33 mg, 57%) was obtained from [Ru(CH=CHPh)Cl-(CO)(PPh$_3$)$_2$] (50 mg). IR (KBr/Nujol): 1921 (ν(CO)), 1551, 1258, 886 cm^{-1}. IR (CH_2Cl_2): 1942 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): 31.6 ppm. ^{1}H NMR ($CDCl_3$): 0.91 (t, CH_2CH_3, 3H, J_{HH} = 7.6 Hz), 1.73 (s, Me^3, 3H), 1.82 (s, Me^5, 3H), 2.09 (q, CH_2CH_3, 2H, J_{HH} = 7.6 Hz), 5.84 (d, Hβ, 1H, J_{HH} = 17.1 Hz), 6.69 (d, *o*-C_6H_5, 2H, J_{HH} = 7.4 Hz), 6.88 (t, *p*-C_6H_5, 1H, J_{HH} = 7.2 Hz), 7.06 (t, *m*-C_6H_5, 2H, J_{HH} = 7.6 Hz), 7.12−7.31 (m, PC_6H_5, 30H), 7.46 (s, CSH, 1H), 8.55 (dt, Hα, 1H, J_{HH} = 17.1, J_{HP} = 3.1 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 923 (55) [M]$^+$, 820 (34) [M − alkenyl]$^+$, 661 (100) [M − PPh$_3$]$^+$, 633 (96) [M − CO − PPh$_3$]$^+$, 530 (85) [M − alkenyl − CO − PPh$_3$]$^+$. Anal. Calcd for $C_{54}H_{49}NOP_2RuS\cdot {}^1/_3CH_2Cl_2$: C, 68.6; H, 5.3; N, 1.5. Found: C, 68.6; H, 5.2; N, 1.4.

[Ru(CH=CHC$_6$H$_4$CH$_3$-4)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (4). The red-orange product (72 mg, 73%) was obtained from [Ru-(CH=CHC$_6$H$_4$CH$_3$-4)Cl(CO)(BTD)(PPh$_3$)$_2$] (150 mg). IR (KBr/Nujol): 1923, 1931 (ν(CO)), 1549, 1261, 912, 835 cm^{-1}. IR (CH_2Cl_2): 1927 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): 31.6 ppm. ^{1}H NMR ($CDCl_3$): 0.92 (t, CH_2CH_3, 3H, J_{HH} = 7.6 Hz), 1.74 (s, Me^3, 3H), 1.84 (s, Me^5, 3H), 2.10 (q, CH_2CH_3, 2H, J_{HH} = 7.6 Hz), 2.25 (s, $C_6H_4CH_3$, 3H), 5.79 (d, Hβ, 1H, J_{HH} = 17.0 Hz), 6.62, 6.90 ((AB)$_2$, C_6H_4, 4H, J_{AB} = 7.8 Hz), 7.13−7.28 (m, PC_6H_5, 30H), 7.42 (s, CSH, 1H), 8.45 (dt, Hα, 1H, J_{HH} = 17.0, J_{HP} = 3.1 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): 10.4 (s, Me^3), 15.0 (s, CH_2CH_3), 17.2 (s, Me^5), 18.3 (s, CH_2CH_3), 21.0 (s, $C_6H_4CH_3$), 124.1 (s, *o*-C_6H_4), 127.3 (t^v, *o*/*m*-PC_6H_5, J_{CP} = 4.4 Hz), 128.4 (s, *m*-C_6H_4), 128.9 (s, *p*-PC_6H_5), 132.5 (s, *p*-C_6H_4), 133.0 (s, Cβ), 133.2 (t^v, *ipso*-PC_6H_5, J_{CP} = 20.5 Hz), 134.2 (t^v + s, *o*/*m*-PC_6H_5 + C,[4] J_{CP} = 5.0 Hz), 139.3 (s, C^3), 139.5 (s, *ipso*-C_6H_4), 148.8 (t, Cα, J_{CP} = 14.1 Hz), 156.7 (s, C^2), 158.6 (s, CSH), 163.7 (s, C^5), 205.8 (t, CO, J_{CP} = 13.5 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 937 (40) [M]$^+$, 820 (23) [M − alkenyl]$^+$, 675 (92) [M − PPh$_3$]$^+$, 647 (80) [M − CO − PPh$_3$]$^+$, 558 (23) [M − alkenyl − PPh$_3$]$^+$, 530 (86) [M − alkenyl − CO − PPh$_3$]$^+$. Anal. Calcd for $C_{55}H_{51}NOP_2RuS\cdot 0.25CH_2Cl_2$: C, 69.3; H, 5.4; N, 1.5. Found: C, 69.4; H, 5.4; N, 1.5.

[Ru(CH=CH^{t}Bu)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (5). The orange product (81 mg, 69%) was obtained from [Ru(CH=CH^{t}Bu)Cl(CO)-(PPh$_3$)$_2$] (100 mg). IR (KBr/Nujol): 1927, 1917 (ν(CO)), 1551, 1256, 910, 864 cm^{-1}. IR (CH_2Cl_2): 1919 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): 30.7 ppm. ^{1}H NMR ($CDCl_3$): 0.57 (s, CMe$_3$, 9H), 0.91 (t, CH_2CH_3, 3H, J_{HH} = 7.5 Hz), 1.71 (s, Me^3, 3H), 1.78 (s, Me^5, 3H), 2.08 (q, CH_2CH_3, 2H, J_{HH} = 7.5 Hz), 5.01 (dt, Hβ, 1H, J_{HH} = 16.7 Hz, J_{HP} = 1.8 Hz), 7.00 (dt, Hα, 1H, J_{HH} = 16.7, J_{PH} = 2.9 Hz), 7.13−7.95 (m, PC_6H_5, 30H), 7.41 (s, CSH, 1H) ppm. FAB-MS (*m/z* (abundance, %)): 902 (3) [M]$^+$, 819 (1) [M − alkenyl]$^+$, 640 (2) [M − PPh$_3$]$^+$, 612 (5) [M − CO − PPh$_3$]$^+$, 557 [M − alkenyl − PPh$_3$]$^+$, 529 (2) [M − alkenyl − CO − PPh$_3$]$^+$. Anal. Calcd for $C_{52}H_{53}NOP_2RuS$: C, 69.2; H, 5.9; N, 1.6. Found: C, 69.4; H, 5.8; N, 1.5.

[Ru{C(C≡CPh)=CHPh}(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (6). The pale brown product (80 mg, 70%) was obtained from [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh$_3$)$_2$] (100 mg). IR (KBr/Nujol): 2163 (ν(C≡C)), 1927 (ν(CO)), 1256, 862 cm^{-1}. IR (CH_2Cl_2): 2158 (ν(C≡C)), 1927 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): 32.4 ppm. ^{1}H NMR ($CDCl_3$): 0.86 (t, CH_2CH_3, 3H, J_{HH} = 7.4 Hz), 1.68 (s, Me^3, 3H), 1.89 (s, Me^5, 3H), 2.07 (q, CH_2CH_3, 2H, J_{HH} = 7.4 Hz), 6.95 (m, =CH, 1H), 7.06−7.49 (m, PC_6H_5 + C_6H_5, 30H + 10H), ppm. FAB-MS (*m/z* (abundance, %)): 1022 (9) [M]$^+$, 856 (1) [M−L$_4$]$^+$, 819 (14) [M − alkenyl]$^+$, 760 (18) [M − PPh$_3$]$^+$, 732 (100) [M − CO − PPh$_3$]$^+$, 530 (43) [M − alkenyl − CO − PPh$_3$]$^+$, 470 (42) [M − CO − 2PPh$_3$]$^+$. Anal. Calcd for $C_{62}H_{53}NOP_2RuS\cdot 0.5CH_2Cl_2$: C, 70.4; H, 5.1; N, 1.3. Found: C, 70.7; H, 5.1; N, 1.3.

[Os(CH=CH$_2$)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (7). The pale red product (47 mg, 60%) was obtained from [Os(CH=CH$_2$)Cl(CO)-(BTD)(PPh$_3$)$_2$] (79 mg). IR (KBr/Nujol): 1915, 1892 (ν(CO)), 1553, 1258, 908, 866 cm^{-1}. IR (CH_2Cl_2): 1904 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): 0.8 ppm. ^{1}H NMR ($CDCl_3$): 0.89 (t, CH_2CH_3, 3H, J_{HH} = 7.6 Hz), 1.57 (s, Me^5, 3H), 1.93 (s, Me^3, 3H), 2.03 (q, CH_2CH_3, 2H, J_{HH} = 7.5 Hz), 5.02 (dd, Hβ, 1H, $J_{H\beta H\alpha}$ = 18.5, $J_{H\beta H\beta'}$ = 1.9 Hz), 6.03 (dd, Hβ' 1H, $J_{H\beta' H\alpha}$ = 11.9, $J_{H\beta' H\beta}$ = 2.0 Hz), 7.06−7.70 (m, C_6H_5, 30H), 7.44 (s, CSH, 1H), 8.64 (ddt, Hα, 1H, $J_{H\alpha H\beta}$ = 18.5, $J_{H\alpha H\beta'}$ = 11.9 Hz, $J_{H\alpha P}$ unresolved) ppm. FAB-MS (*m/z* (abundance, %)): 937 (2) [M]$^+$, 675 (5) [M − PPh$_3$]$^+$. Anal. Calcd for $C_{48}H_{45}NOOsP_2S\cdot 0.5CH_2Cl_2$: C, 59.5; H, 4.7; N, 1.4. Found: C, 59.6; H, 4.8; N, 1.4.

[Ru(CH=CHCPh$_2$OH)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (8). The pale orange product (75 mg, 75%) was obtained from [Ru-(CH=CHCPh$_2$OH)Cl(CO)(BTD)(PPh$_3$)$_2$] (100 mg). IR (KBr/Nujol): 1923 (ν(CO)), 1556, 1256, 910, 864 cm^{-1}. IR (CH_2Cl_2): 1923 (ν(CO)) cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): 32.0 ppm. ^{1}H NMR ($CDCl_3$): 0.97 (t, CH_2CH_3, 3H, J_{HH} = 7.5 Hz), 1.27 (s, OH, 1H), 1.60 (s, Me^3, 3H), 1.75 (s, Me^5, 3H), 2.12 (q, CH_2CH_3, 2H, J_{HH} = 7.5 Hz), 5.89 (d, Hβ, 1H, J_{HH} = 16.7 Hz), 6.87 (d, *o*-C_6H_5, 2H, J_{HH} = 6.2 Hz), 7.10−7.95 (m, PC_6H_5 + C_6H_5 + CSH, 30H + 8H + 1H), 7.49 (dt, Hα, 1H, J_{HH} = 16.7, J_{HP} = 2.3 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 1028 (2) [M]$^+$, 1011 (2) [M − OH]$^+$, 766 (2) [M − PPh$_3$]$^+$, 749 (3) [M − OH − PPh$_3$]$^+$, 557 (2) [M − alkenyl − PPh$_3$]$^+$, 529 (2) [M − alkenyl − CO − PPh$_3$]$^+$. Anal. Calcd for $C_{61}H_{55}NO_2P_2RuS\cdot 1.25CH_2Cl_2$: C, 65.9; H, 5.1; N, 1.2. Found: C, 66.1; H, 4.8; N, 1.1.

[Ru(=CHCH=CPh$_2$)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$]BF$_4$ (9). [Ru-(CH=CHCPh$_2$OH)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**10**; 36 mg, 0.035 mmol) was suspended in diethyl ether (10 mL) and $HBF_4\cdot OEt_2$ (2 drops, excess) added, causing an immediate color change from orange to dark red. The reaction mixture was stirred for 10 min, and the precipitate was filtered and washed with diethyl ether (10 mL) and hexane (10 mL) and dried. The dark red product can be recrystallized from dichloromethane and diethyl ether. Yield: 33 mg (86%). IR (KBr/Nujol): 1965 (ν(CO)),

1568 (ν(Ru=CC=C)), 1252, 1055 (ν(B−F)), 903, 856 cm^{-1}. IR (CH_2Cl_2): 1971 (ν(CO)), 1565 (ν(Ru=CC=C)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 28.6 ppm. ^1H NMR ($CDCl_3$): 0.96 (t, CH_2CH_3, 3H, J_{HH} = 7.5 Hz), 1.56 (s, Me^3, 3H), 1.87 (s, Me^5, 3H), 2.18 (q, CH_2CH_3, 2H, J_{HH} = 7.5 Hz), 6.45 (d, *o*-CC_6H_5, 2H, J_{HH} = 7.3 Hz), 7.01−7.96 (m, PC_6H_5 + C_6H_5 + CSH, 30H + 8H + 1H), 8.40 (d, RuC=CH, 1H, J_{HH} = 14.1 Hz), 16.00 (dt, Ru=CH, 1H, J_{HH} = 14.1, J_{HP} = 2.6 Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 10.7 (s, Me^3), 14.8 (s, CH_2CH_3), 17.1 (s, Me^5), 18.5 (s, CH_2CH_3), 128.8−134.7 (C_6H_5 + C^4), 137.8 (s, C^3), 149.2 (s, Cβ), 157.0 (s, C^2), 158.1 (s, CSH), 159.8 (s, C^5), 168.0 (s, Cγ), 201.0 (t, CO, J_{CP} = 13.4 Hz), 316.3 (t, Cα, J_{CP} = 10.8 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 1012 (5) [M]$^+$, 820 (3) [M − carbene]$^+$, 750 (9) [M − PPh_3]$^+$. Anal. Calcd for $C_{61}H_{54}BF_4NOP_2RuS\cdot0.75CH_2Cl_2$: C, 63.8; H, 4.8; N, 1.2. Found: C, 64.1; H, 4.7; N, 1.0.

[Ru{CH=CH(HO)C_6H_{10}}(κ^2-L_4)(CO)(PPh_3)$_2$] (10). [Ru{CH=CH(HO)C_6H_{10}}Cl(CO)(BTD)(PPh_3)$_2$] (80 mg, 0.084 mmol) and **HL_4** (14 mg, 0.084 mmol) were suspended in dichloromethane (20 mL) to give a deep red solution. An ethanolic solution (15 mL) of sodium methoxide (4.6 mg, 0.085 mmol) was added, causing a color change to pale orange. The mixture was stirred for 1.5 h and the solvent volume reduced to ca. 5 mL. This was cooled to −20 °C until precipitation of a bright orange product was complete. This was washed with water (5 mL), cold ethanol (10 mL), and hexane (10 mL). The product is slightly soluble in ethanol but can be recrystallized from dichloromethane−ethanol mixtures. Yield: 54 mg (68%). IR (KBr/Nujol): 1931 (ν(CO)), 1549, 1258, 907, 860 cm^{-1}. IR (CH_2Cl_2): 1927 (ν(CO)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 28.8 ppm. ^1H NMR ($CDCl_3$): 1.01 (t, CH_2CH_3, 3H, J_{HH} = 7.6 Hz), 1.17−1.37 (m, Cy, 10H), 1.26 (s, OH, 1H), 1.67 (s, Me^3, 3H), 1.84 (s, Me^5, 3H), 2.16 (q, CH_2CH_3, 2H, J_{HH} = 7.6 Hz), 5.37 (dt, Hβ, 1H, J_{HH} = 17.2 Hz, J_{HP} = 2.0 Hz), 7.07 (s, CSH, 1H), 7.15−7.32 [m, PC_6H_5, 30H), 7.36 (dt, Hα, 1H, J_{HH} = 17.2, J_{HP} = 2.5 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 928 (22) [M − H_2O]$^+$, 820 (25) [M − alkenyl]$^+$, 666 (37) [M − H_2O − PPh_3]$^+$, 638 (21) [M − H_2O − CO − PPh_3]$^+$, 558 (22) [M − alkenyl − PPh_3]$^+$, 530 (100) [M − alkenyl − CO − PPh_3]$^+$. Anal. Calcd for $C_{54}H_{55}NO_2P_2RuS\cdot0.2CH_2Cl_2$: C, 67.7; H, 5.8; N, 1.5. Found: C, 67.8; H, 6.0; N, 1.4.

[Ru(C_6H_5)(κ^2-L_4)(CO)(PPh_3)$_2$] (11). The orange product (43 mg, 74%) was obtained from [Ru(C_6H_5)Cl(CO)(PPh_3)$_3$] (50 mg). IR (NaCl/Nujol): 1925 (ν(CO)), 1545, 1250, 897, 848 cm^{-1}. IR (CH_2Cl_2): 1919 (ν(CO)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 32.8 ppm. ^1H NMR ($CDCl_3$): 0.78 (t, CH_2CH_3, 3H, J_{HH} = 7.5 Hz), 1.70 (s, Me^3, 3H), 1.91 (s, Me^5, 3H), 1.92 (q, CH_2CH_3, 2H, J_{HH} = 7.5 Hz), 6.53 (t, *m*-C_6H_5, 2H, J_{HH} = 7.0 Hz), 6.63 (t, *p*-C_6H_5, 1H, J_{HH} = 7.0 Hz), 7.07, 7.24 (m × 2, PC_6H_5 + *o*-C_6H_5, 30H + 2H), 7.68 (s, CSH, 1H) ppm. FAB-MS (*m/z* (abundance, %)): 895 (20) [M]$^+$, 818 (24) [M − C_6H_5]$^+$, 729 (4) [M − L_4]$^+$, 633 (68) [M − PPh_3]$^+$, 606 (100) [M − CO − PPh_3]$^+$, 557 (17) [M − C_6H_5 − PPh_3]$^+$, 529 (63) [M − C_6H_5 − CO − PPh_3]$^+$. Anal. Calcd for $C_{52}H_{47}NOP_2RuS\cdot CH_2Cl_2$: C, 64.8; H, 5.0; N, 1.4. Found: C, 64.6; H, 4.8; N, 1.0.

[Ru(C≡CPh)(κ^2-L_4)(CO)(PPh_3)$_2$] (12). [Ru(C≡CPh)Cl(CO)(BTD)(PPh_3)$_3$] (62 mg, 0.067 mmol) and **HL_4** (13 mg, 0.078 mmol) were suspended in dichloromethane (20 mL) and treated with sodium methoxide (7 mg, 0.130 mmol) in ethanol (10 mL). This gave rise to a color change from intense red to red-brown. The mixture was stirred for 1 h and all solvent removed and the residue dissolved in dichloromethane and filtered through diatomaceous earth to remove NaCl. The solvent was removed and the solid triturated ultrasonically in hexane (10 mL) to provide a deep red product. This was washed with hexane (10 mL) and dried. Yield: 51 mg (83%). IR (KBr/Nujol): 2097 (ν(C≡C)), 1946 (ν(CO)), 1556, 1254, 914, 866 cm^{-1}. IR (CH_2Cl_2): 2098 (ν(C≡C)), 1942 (ν(CO)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 38.3 ppm. ^1H NMR ($CDCl_3$): 0.89 (t, CH_2CH_3, 3H, J_{HH} = 7.6 Hz), 1.54 (s, Me^3, 3H), 1.95 (s, Me^5, 3H), 1.98 (q, CH_2CH_3, 2H, J_{HH} = 7.6 Hz), 6.86 (d, *o*-C_6H_5, 2H, J_{HH} = 7.6 Hz), 6.98 (t, *p*-C_6H_5, 1H, J_{HH} = 7.6 Hz), 7.09 (t, *m*-C_6H_5, 2H, J_{HH} = 7.6 Hz), 7.60 (s, CSH, 1H), 7.19−7.86 (m, PC_6H_5, 30H) ppm. FAB-MS (*m/z* (abundance, %)): 920 (17) [M]$^+$, 819 (5) [M − C≡CPh]$^+$, 653 (10) [M − C≡CPh − **L_4**]$^+$, 630 (28) [M − CO − PPh_3]$^+$, 529 (13) [Ru(**L_4**)(PPh_3)]$^+$. Anal. Calcd for $C_{54}H_{47}NOP_2RuS$: C, 70.4; H, 5.1; N, 1.5. Found: C, 70.0; H, 4.9; N, 1.4.

[RuH(κ^2-L_6)(CO)(PPh_3)$_2$] (13). Yellow crystalline product (70 mg, 77%) obtained from [RuHCl(CO)(BTD)(PPh_3)$_2$] (100 mg). IR (KBr/Nujol): 1925 (ν(CO)), 1563 (ν(C=O)) cm^{-1}. IR (CH_2Cl_2): 1920 (ν(CO)), 1563 (ν(C=O)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 47.5 ppm. ^1H NMR ($CDCl_3$, 500.13 MHz): −9.99 (t, RuH, 1H, J_{PH} = 20.5 Hz), 6.02 (dd, H^4, 1H, J_{HH} = 4.1, 1.2 Hz), 6.53 (d, H^3, 1H, J_{HH} = 4.1 Hz), 6.80 (s (br), H^5, 1H), 7.22−7.46 (m, C_6H_5, 30H), 7.55 (q, CHO, 1H, $J_{HH} \approx J_{HP}$ = 1.3 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 748 (8) [M]$^+$, 625 (1) [M − CO − **L_6**]$^+$, 363 (5) [RuPPh$_3$]$^+$. Anal. Calcd for $C_{42}H_{35}NO_2P_2Ru$: C, 67.4; H, 4.7; N, 1.9. Found: C, 67.0; H, 4.7; N, 1.8.

[Ru(CH=CH_2)(κ^2-L_6)(CO)(PPh_3)$_2$] (14). The yellow product (70 mg, 65%) was obtained from [Ru(CH=CH_2)Cl(CO)(PPh_3)$_2$] (100 mg). IR (KBr/Nujol): 1911 (ν(CO)), 1568 (ν(C=O)) cm^{-1}. IR (CH_2Cl_2): 1918 (ν(CO)), 1568 (ν(C=O)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 37.0 ppm. ^1H NMR (CD_2Cl_2): 5.12 (ddt, Hβ, 1H, $J_{H\beta H\alpha}$ = 18.1, $J_{H\beta H\beta'}$ = 2.9 Hz, $J_{H\beta P}$ = 1.9 Hz), 5.41 (ddt, Hβ' 1H, $J_{H\beta' H\alpha}$ = 11.0, $J_{H\beta' H\beta}$ = 2.8 Hz, $J_{H\beta' P}$ = 2.2 Hz), 6.05 (dd, H^4, 1H, J_{H4H3} = 4.1 Hz, J_{H4H5} = 1.3 Hz), 6.62 (dd, H^3, 1H, J_{H3H4} = 4.1 Hz, J_{H3H5} = 1.0 Hz), 6.92 (dd, H^5, 1H, J_{H5H4} = 1.3 Hz, J_{H5H3} = 1.0 Hz), 7.19−7.33 (m, C_6H_5, 30H), 7.53 (q, CHO, 1H, $J_{HH} \approx J_{HP}$ = 1.3 Hz), 7.71 (ddt, Hα, 1H, $J_{H\alpha H\beta}$ = 18.1, $J_{H\alpha H\beta'}$ = 11.0 Hz, $J_{H\alpha P}$ = 2.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 116.8 (s, C^4), 121.3 (s (br), Cβ), 122.7 (s, C^3), 128.0 (t^v, *o*/*m*-PC_6H_5, J_{CP} = 4.6 Hz), 129.9 (s, *p*-PC_6H_5), 132.2 (t^v, *ipso*-PC_6H_5, J_{CP} = 21.1 Hz), 134.5 (t^v, *o*/*m*-PC_6H_5, J_{CP} = 5.4 Hz), 144.7 (s, C^2), 146.5 (s, C^5), 160.3 (t, Cα, J_{CP} = 12.9 Hz), 177.6 (s, CHO), 208.7 (t, CO, J_{CP} = 15.5 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 774 (55) [M]$^+$, 747 (36) [M − CO]$^+$, 512 (100) [M − PPh_3]$^+$, 485 (47) [M − alkenyl − CO − PPh_3]$^+$, 457 (36) [M − alkenyl − CO − PPh_3]$^+$, 390 (20) [Ru(alkenyl)PPh_3]$^+$, 363 (60) [RuPPh$_3$]$^+$. Anal. Calcd for $C_{44}H_{37}NO_2P_2Ru\cdot 0.75CH_2Cl_2$: C, 64.1; H, 4.6; N, 1.7. Found: C, 64.1; H, 4.6; N, 1.7.

[Ru(CH=$CHC_6H_4CH_3$-4)(κ^2-L_6)(CO)(PPh_3)$_2$] (15). The yellow product (84 mg, 92%) was obtained from [Ru(CH=$CHC_6H_4CH_3$-4)Cl(BTD)(CO)(PPh_3)$_2$] (100 mg). IR (KBr/Nujol): 1917 (ν(CO)), 1558 (ν(C=O)) cm^{-1}. IR (CH_2Cl_2): 1920 (ν(CO)), 1568 (ν(C=O)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.2 ppm. ^1H NMR ($CDCl_3$): 2.21 (s, CH_3, 3H), 6.04 (d, Hβ, 1H, J_{HH} = 16.8 Hz), 6.06 (dd, H^4, 1H, J_{H4H3} = 4.1 Hz, J_{H4H5} = 1.3 Hz), 6.42, 6.82 ((AB)$_2$, 4H, J_{AB} = 8.0 Hz), 6.62 (d, H^3, 1H, J_{H3H4} = 4.1 Hz), 6.96 (s (br), H,^{5} 1H), 7.18−7.31 (m, C_6H_5, 30H), 7.71 (s, CHO, 1H, $J_{HH} \approx J_{HP}$ = 1.3 Hz), 8.08 (dt, Hα, 1H, J_{HH} = 16.8, J_{HP} = 3.1 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 865 (20) [M]$^+$, 748 (16) [M − alkenyl]$^+$, 603 (100) [M − PPh_3]$^+$, 575 (52) [M − CO − PPh_3]$^+$, 480 (16) [M − CO − **L_6** − PPh_3]$^+$, 458 (25) [M − alkenyl − CO − PPh_3]$^+$. Anal. Calcd for $C_{51}H_{43}NO_2P_2Ru$: C, 70.8; H, 5.0; N, 1.6. Found: C, 70.7; H, 5.0; N, 1.6.

[Ru{C(C≡CPh)=CHPh}(κ^2-L_6)(CO)(PPh_3)$_2$] (16). The yellow product (90 mg, 85%) was obtained from [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh_3)$_2$] (100 mg). IR (KBr/Nujol): 2156 (ν(C≡C)), 1921 (ν(CO)), 1568 (ν(C=O)) cm^{-1}. IR (CH_2Cl_2): 2161 (ν(C≡C)), 1925 (ν(CO)), 1566 (ν(C=O)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 35.0 ppm. ^1H NMR ($CDCl_3$): 5.97 (dd, H,^{4} 1H, J_{H4H3} = 4.1 Hz, J_{H4H5} unresolved), 6.50 (dd, H^3, 1H, J_{H3H4} = 4.1 Hz, J_{H3H4} unresolved), 6.92 (s, RuC=CH, 1H), 6.95 (s (br), H,^{5} 1H), 7.05−7.37 (m, PC_6H_5 + C_6H_5, 30H +10H), 7.65 (s (br), CHO, 1H) ppm. FAB-MS (*m/z* (abundance, %)): 950 (34) [M]$^+$, 856 (8) [M − L_6]$^+$, 747 (25) [M − alkenyl]$^+$, 688 (12) [M − PPh_3]$^+$, 660 (100) [M − CO − PPh_3]$^+$, 564 (8) [M − L_6 − CO − PPh_3]$^+$. Anal. Calcd for $C_{58}H_{45}NO_2P_2Ru$: C, 73.3; H, 4.8%; N, 1.5. Found: C, 72.9; H, 4.7; N, 1.4.

Table 1. Crystal Data for Compounds HL_4, 2, 6, and 15

	HL_4	2	6	15
chem formula	$C_9H_{13}NS$	$C_{48}H_{45}NOP_2RuS$	$C_{62}H_{53}NOP_2RuS$	$C_{51}H_{43}NO_2P_2Ru$
fw	167.26	846.92	1023.12	864.87
cryst color	pale yellow	orange	orange	yellow
cryst size (mm)	0.08 × 0.04 × 0.04	0.34 × 0.32 × 0.10	0.34 × 0.30 × 0.14	0.41 × 0.18 × 0.16
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	7.9524(18)	10.7792(5)	49.254(3)	10.9041(5)
b/Å	13.352(3)	12.3603(6)	9.4757(6)	14.0150(6)
c/Å	8.6274(19)	16.5312(8)	23.9076(15)	15.4302(7)
α/deg	90	74.5650(10)	90	87.2290(10)
β/deg	94.698(4)	76.5140(10)	116.9170(10)	75.6060(10)
γ/deg	90	72.9860(10)	90	67.2240(10)
V/Å^3	913.0(4)	2001.13(17)	9949.3(11)	2102.91(16)
Z	4	2	8	2
calcd density (g/cm^3)	1.217	1.406	1.366	1.366
μ(Mo Kα)/mm^{-1}	0.291	0.562	0.466	0.491
F(000)	360	876	4240	892
no. of params	100	487	613	514
no. of rflns collected	7759	17 865	43 093	18 753
no. of unique reflns (R_{int})	2172 (0.0437)	9249 (0.0168)	11 947 (0.0485)	9699 (0.0177)
R1 ($I > 2\sigma(I)$)	0.0591	0.0359	0.0468	0.0618
wR2 (all data)	0.1416	0.0925	0.1029	0.1416
resid (max, min)/e Å^{-3}	0.480, −0.417	2.143, −0.648	0.801, −0.790	5.447,[a] −1.864

[a] Close to Ru, second highest 1.2 e Å^{-3}.

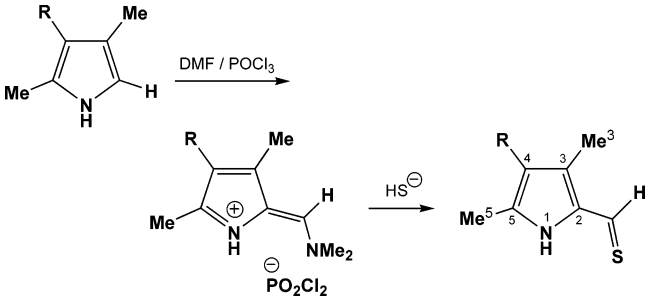
[Os(CH=CH$_2$)(κ^2-L_6)(CO)(PPh$_3$)$_2$] (17). The red product (61 mg, 83%) was obtained from [Os(CH=CH$_2$)Cl(CO)(BTD)(PPh$_3$)$_2$] (80 mg). IR (KBr/Nujol): 1896 (ν(CO)), 1568 (ν(C=O)) cm^{-1}. IR (CH_2Cl_2): 1892 (ν(CO)), 1570 (ν(C=O)) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 11.4 ppm. ^1H NMR ($CDCl_3$): 5.08 (ddt, Hβ, 1H, $J_{H\beta H\alpha}$ = 18.5, $J_{H\beta H\beta'}$ = 3.7 Hz, $J_{H\beta P}$ = 2.1 Hz), 5.68 (ddt, Hβ' 1H, $J_{H\beta' H\alpha}$ = 11.9 Hz, $J_{H\beta' H\beta}$ = 3.6 Hz, $J_{H\beta' P}$ = 2.6 Hz), 5.98 (dd, H^4, 1H, J_{H4H3} = 4.2 Hz, J_{H4H5} = 1.2 Hz), 6.59 (d, H^3, 1H, J_{H3H4} = 4.1 Hz), 6.62 (s (br), H^5, 1H), 7.19−7.53 (m, C_6H_5, 30H), 7.64 (q, CHO, 1H, $J_{HH} \approx J_{HP}$ = 1.3 Hz), 8.20 (ddt, Hα, 1H, $J_{H\alpha H\beta}$ = 18.5 Hz, $J_{H\alpha H\beta'}$ = 11.9 Hz, $J_{H\alpha P}$ = 2.1 Hz) ppm. FAB-MS (*m/z* (abundance, %)): 863 (22) [M]$^+$, 835 (23) [M − CO]$^+$, 740 (2) [M − **L_6** − CO]$^+$, 602 (100) [M − PPh$_3$]$^+$, 575 (8) [M − CO − PPh$_3$]$^+$. Anal. Calcd for $C_{44}H_{37}NO_2OsP_2$: C, 57.9; H, 4.1; N, 1.5. Found: C, 58.1; H, 4.2; N, 1.4.

Crystallography. Slow evaporation of a benzene solution of **HL_4** yielded suitable crystals for X-ray diffraction, while crystals of [Ru(CH=CH$_2$)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**2**), [Ru{C(C≡CPh)=CHPh}(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**6**), and [Ru(CH=CHC$_6$H$_4$-CH$_3$-4)(κ^2-L$_6$)(CO)(PPh$_3$)$_2$] (**15**) were obtained by slow diffusion of ethanol into solutions of the complexes in dichloromethane. Single crystals of compounds **HL_4**, **2**, **6**, and **15** were mounted on glass fibers, and all geometric and intensity data were taken from these samples on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 150 ± 2 K. Data reduction and integration were carried out with SAINT+ and absorption corrections applied using the program SADABS. The structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Structure solution and refinement used the SHELXTL PLUS V6.10 program package.[40] Table 1 provides a summary of the crystal data and data collection and refinement parameters for **HL_4**, **2**, **6**, and **15**.

The crystallographic data for the structures of **HL_4**, **2**, **6**, and **15** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 271247, 271248, 271249, and 271250, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, int. code +44 (1223) 336-033; e-mail for inquiry, fileserv@ccdc.cam.ac.uk).

(40) SHELTXTL Version 6.10, Bruker AXS, 2000.

Scheme 2. Preparation of Pyrrolecarbothioaldehyde Compounds via the Vilsmair Salt



Results and Discussion

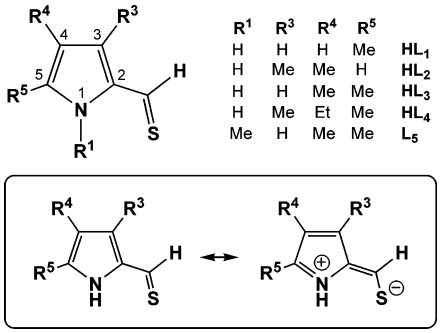
We were inspired by the unusual pyrrolecarbothioaldehyde unit proposed by Woodward and co-workers[3] in their report of the synthesis of chlorophyll to prepare a series of thioaldehyde molecules conjugated to a pyrrole. Once this had been achieved, one representative molecule (**HL_4**) was chosen to investigate the coordination properties of these molecules.

Carbothioaldehyde Ligands. Dimethylformamide solutions of the pyrroles were added to a stirred solution of phosphorus oxychloride to form the Vilsmair salt, which, on treatment with aqueous hydrogen sulfide, provided the carbothioaldehyde products (**HL_1**−**HL_4**) in good yields (66−73%) after workup and chromatography (Scheme 2 and Chart 2).

Only the synthesis of 1,4,5-trimethylpyrrole-2-carbothioaldehyde (**L_5**) failed to proceed in good yield (31%), and the compound was found to decompose readily in air. The substitution at the pyrrole nitrogen appears to diminish the conjugation afforded the thioaldehyde moiety by the pyrrole ring.

The compounds **HL_1**−**HL_4** were characterized by ^1H and $^{13}C\{^1H\}$ NMR and elemental analysis. In the ^1H

Chart 2. Pyrrolecarbothioaldehyde Compounds Prepared in This Work



R^1	R^3	R^4	R^5	
H	H	H	Me	HL_1
H	Me	Me	H	HL_2
H	H	Me	Me	HL_3
H	Me	Et	Me	HL_4
Me	H	Me	Me	L_5

NMR spectrum of 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde (**HL_4**), triplet (1.03 ppm, J_{HH} = 7.6 Hz) and quartet (2.35 ppm, J_{HH} = 7.6 Hz) resonances were observed for the ethyl group, with two singlets attributed to the remaining methyl substituents at 2.15 and 2.21 ppm. To lower field, a broad resonance was observed for the NH proton at 9.34 ppm and a sharp singlet at 10.23 ppm for the CSH proton. Excitation of this latter proton in a nuclear Overhauser enhancement (NOE) experiment led to enhancement of the methyl peak at 2.15 ppm, allowing this resonance to be assigned to the Me^3 protons. The $^{13}C\{^1H\}$ NMR spectrum revealed nine resonances, as expected. The lowest field peak at 190.6 ppm was attributed to the thioaldehyde carbon. The remaining carbon nuclei were assigned using heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond correlation (HMBC) experiments. The absence of resonances at 127.6, 131.0, 141.2, and 142.2 ppm in the HMQC experiment indicated that these were quaternary carbon nuclei, and they were assigned on the basis of HMBC data as resonances for C^4, C^3, C^2, and C^5, respectively. The same experiments were used to assign the resonances in the $^{13}C\{^1H\}$ NMR spectrum at 9.2, 12.1, 14.6, and 17.0 ppm to the Me^3, Me^5, CH_2CH_3, and CH_2CH_3 nuclei, respectively. The spectroscopic features of the other pyrrolecarbothioaldehyde compounds were assigned on the basis of these data. Single crystals of 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde (**HL_4**) were grown by slow evaporation of a concentrated benzene solution. This permitted a structural investigation to be carried out (Figure 1). The structure is examined in detail in the structural discussion.

Alkenyl Complexes. 3,5-Dimethyl-4-ethylpyrrole-2-carbothioaldehyde (**HL_4**) was chosen as a representative compound with which to investigate the coordination chemistry of the thioaldehyde molecules. The substituents on the pyrrole ring (Me, Et) gave rise exclusively to high-field resonances in the ^1H NMR spectrum, preventing overlap with other resonances in the 5−7 ppm range and provided characteristic spectroscopic features with which to identify the presence of the ligand in the complexes.

A dichloromethane−ethanol solution of the hydride starting material $[RuHCl(CO)(PPh_3)_3]$[27] was treated with **HL_4**, leading to a rapid color change from yellow to orange. This was probably due to formation of complexes with monodentate coordination of the **HL_4** ligand, but attempts to isolate these species led to intractable mixtures of products, one of which was identified as $[RuH(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$ (**1**) by $^{31}P\{^1H\}$ NMR. Complete conversion to this complex was achieved by addition of sodium methoxide, suggesting that deprotonation occurs after coordination to the metal center. Reduction in solvent volume led to crystallization of a pale orange solid in good yield (Scheme 3). A second route to **1** was also employed, starting from the 2,1,3-benzothiadiazole (BTD) complex $[RuHCl(CO)(BTD)(PPh_3)_2]$[28] under analogous conditions.

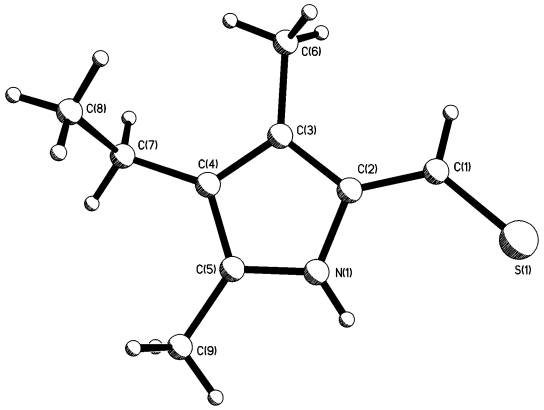
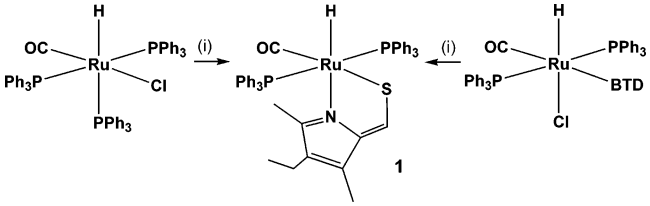


Figure 1. Molecular structure of **HL_4**. Selected bond lengths (Å) and angles (deg): C1−S1 = 1.658(3), C5−N1 = 1.342(3), C2−N1 = 1.388(3), C1−C2 = 1.382(3), C2−C3 = 1.413(3), C3−C4 = 1.396(3), C4−C5 = 1.407(3); C5−N1−C2 = 110.1(2), C2−C1−S1 = 127.6(2), C1−C2−N1 = 124.2(2), N1−C2−C3 = 106.3(2), C4−C3−C2 = 108.1(2), C3−C4−C5 = 106.6(2), N1−C5−C4 = 108.9(2).

Scheme 3[a]

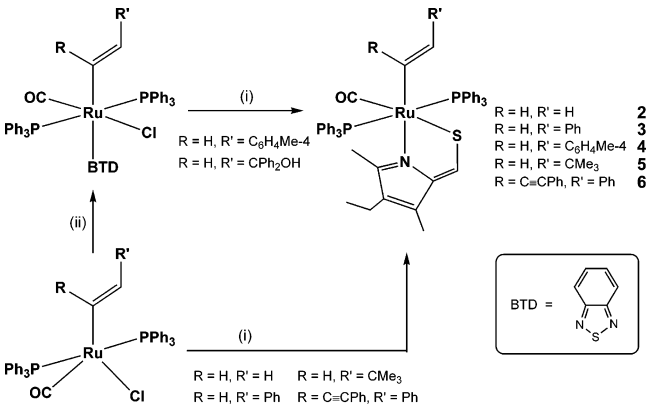


[a] Legend: (i) **HL_4**, NaOMe.

The presence of the carbonyl ligand was confirmed by a ν(CO) absorption at 1919 cm^{-1} in the solid-state infrared spectrum. No ν(RuH) absorption was observed, and this feature was probably obscured by the carbonyl band. The trans arrangement of the phosphines was indicated by a singlet in the ^{31}P NMR spectrum at 17.1 ppm. The ^1H NMR spectrum of the complex showed a high-field hydride triplet resonance at −10.61 ppm with a J_{HP} coupling of 19.9 Hz. Triplet (0.92 ppm, J_{HH} = 7.5 Hz) and quartet (2.01 ppm, J_{HH} = 7.5 Hz) resonances were observed for the ethyl substituent of the **L_4** ligand, while two singlets at 1.62 and 1.70 ppm were attributed to the remaining methyl groups. The thioaldehyde CSH proton was observed as a singlet resonance at 7.01 ppm, a value dramatically shifted upfield from the corresponding feature in the free ligand (10.27 ppm). A molecular ion at *m/z* 821 was observed in the FAB mass spectrum with fragmentation due to loss of the **L_4** ligand at *m/z* 654. Elemental analysis confirmed the overall composition of the complex.

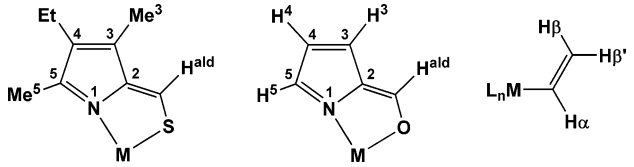
Reaction of the 16-electron complex $[Ru(CH{=}CH_2)Cl(CO)(PPh_3)_2]$[30] with **$HL_4$** in the presence of sodium methoxide led to isolation of a crystalline red-brown solid in moderate yield (Scheme 4).

Scheme 4[a]



[a] Legend: (i) **HL$_4$**, NaOMe; (ii) BTD (2,1,3-benzothiadiazole).

Chart 3. Numbering Scheme for the HL$_4$, HL$_6$, and Ethenyl Ligands



The alkenyl ligand gives rise to three doublet of doublet of triplet resonances in the ^{1}H NMR spectrum. A peak at 4.88 ppm was observed for the vinylic β-proton (Chart 3) showing couplings to the Hα proton ($J_{H\beta H\alpha}$ = 18.2 Hz), the β'-proton ($J_{H\beta H\beta'}$ = 3.5 Hz), and the two phosphines ($J_{H\beta P}$ = 1.5 Hz). The resonance at 5.64 ppm (ddt, $J_{H\beta' H\alpha}$ = 10.8, $J_{H\beta' H\beta}$ = 3.5 Hz, $J_{H\beta' P}$ = 2.0 Hz) was assigned to the β' proton, while the lowest field resonance at 8.04 ppm (ddt, $J_{H\alpha H\beta}$ = 18.2, $J_{H\alpha H\beta'}$ = 10.8 Hz, $J_{H\alpha P}$ = 2.9 Hz) was attributed to the α proton. The resonances associated with the pyrrolecarbothioaldehyde ligand were similar to those for complex **1**, except that the CSH resonance was obscured by the aromatic region.

The overall composition was given by the molecular ion in the FAB mass spectrum at *m/z* 846 and elemental analysis of the crystals as a hemisolvate. This was confirmed by an X-ray crystal structure obtained from single crystals of [Ru(CH=CH$_2$)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**2**) grown by slow diffusion of ethanol into a dichloromethane solution of the complex (Figure 2).

The complex [Ru(CH=CHPh)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**3**) was prepared from reaction of [Ru(CH=CHPh)Cl(CO)(PPh$_3$)$_2$] with the deprotonated **L$_4$** ligand, while treatment of [Ru(CH=CHC$_6$H$_4$CH$_3$-4)Cl(CO)(BTD)(PPh$_3$)$_2$] with **HL$_4$** in the presence of base resulted in the displacement of both 2,1,3-benzothiadiazole (BTD) and chloride ligands to yield [Ru(CH=CHC$_6$H$_4$CH$_3$-4)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**4**). The ^{13}C{^{1}H} NMR spectrum of **4** showed that the chemical shifts of the resonances for the substituents on the pyrrole ring differed only slightly from those in the free ligand. As expected, those associated with the ring itself were shifted to a much greater degree. The greatest shift was found for the CSH proton at 158.6 ppm, which resonated at 190.6 ppm in the spectrum of **HL$_4$**. Two triplet resonances were observed for the carbon monoxide ligand (205.8 ppm, J_{CP} = 13.5 Hz) and the α carbon of the alkenyl ligand (148.8 ppm, J_{CP} = 14.1 Hz).

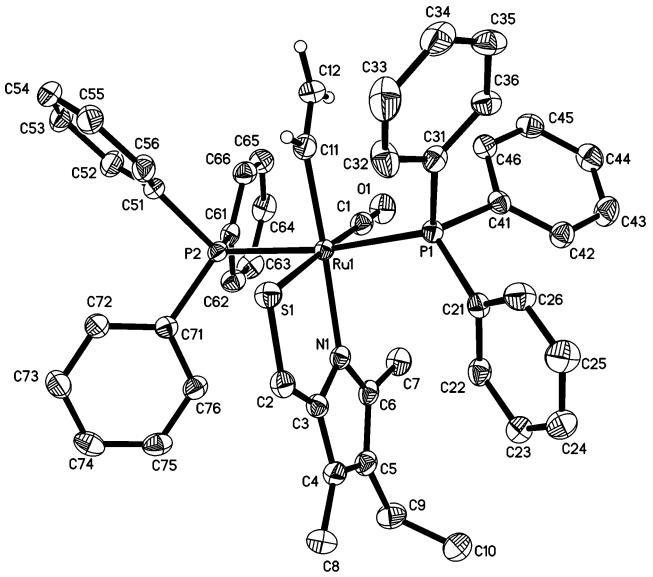


Figure 2. Molecular structure of [Ru(CH=CH$_2$)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**2**). Selected bond lengths (Å) and angles (deg): Ru1−C1 = 1.848(2), Ru1−C11 = 2.083(2), Ru1−N1 = 2.1739(18), Ru1−P2 = 2.3843(5), Ru1−P1 = 2.3987(6), Ru1−S1 = 2.4536(6), S1−C2 = 1.706(2), N1−C3 = 1.403(3), C2−C3 = 1.368(3), C11−C12 = 1.330(3); P2−Ru1−P1 = 171.605(19), C1−Ru1−C11 = 89.96(10), C1−Ru1−N1 = 96.72(8), C1−Ru1−P2 = 89.69(7), C11−Ru1−P2 = 87.59(6), N1−Ru1−P2 = 93.50(5), C1−Ru1−P1 = 91.80(7), C11−Ru1−P1 = 84.15(6), N1−Ru1−P1 = 94.53(5), C11−Ru1−S1 = 93.14(7), P2−Ru1−S1 = 89.32(2), P1−Ru1−S1 = 89.64(2), N1−Ru1−S1 = 80.20(5), C2−C3−N1 = 119.8(2), C12−C11−Ru1 = 131.31(19).

A further example, [Ru(CH=CH^{t}Bu)(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**5**), was prepared from the coordinatively unsaturated precursor [Ru(CH=CH^{t}Bu)Cl(CO)(PPh$_3$)$_2$]. A singlet integrated for nine protons was observed in the ^{1}H NMR spectrum at 0.57 ppm (CMe$_3$), indicating the retention of the alkenyl ligand. In common with the other complexes discussed here, the solid-state infrared spectrum of **5** showed bands at 1551, 1256, 910, and 864 cm^{-1}. These correlate well with the major spectroscopic features of the **HL$_4$** ligand, which displays bands at 1556, 1261, 1107, 893, and 841 cm^{-1}. The 1107 cm^{-1} absorption is not present in the spectra of the complexes and may be associated with the NH unit in the free ligand.

The enynyl complex [Ru{C(C≡CPh)=CHPh}(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**6**) was prepared by treatment of [RuCl{C(C≡CPh)=CHPh}(CO)(PPh$_3$)$_2$] with 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde (**HL$_4$**) and sodium methoxide. The clearest spectroscopic evidence for retention of the enynyl ligand was the ν(C≡C) absorption at 2163 cm^{-1}. The complex gave rise to a molecular ion in the FAB mass spectrum at *m/z* 1023 with unusual fragmentation due to loss of the **L$_4$** ligand, at *m/z* 856. Single crystals of the complex [Ru{C(C≡CPh)=CHPh}(κ^2-L$_4$)(CO)(PPh$_3$)$_2$] (**6**) were grown from dichloromethane and ethanol. The resulting crystal structure is shown in Figure 3.

To broaden the investigation of this ligand system, an example of an osmium alkenyl complex bearing the **L$_4$** ligand was prepared. Complexes of the type [Os(CH=CHR)Cl(BTD)(CO)(PPh$_3$)$_2$] are accessible from the BTD (2,1,3-benzothiadiazole) complex [OsHCl(BTD)(CO)-

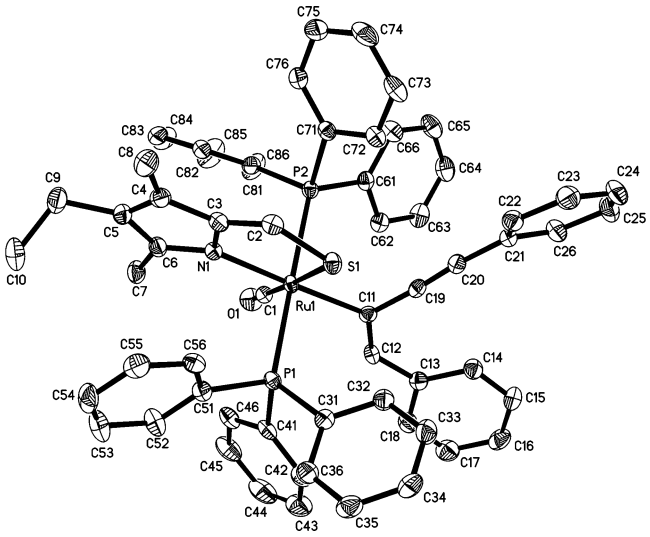
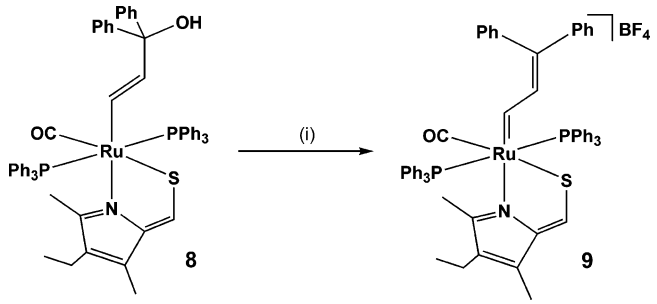


Figure 3. Molecular structure of [Ru{C(C≡CPh)=CHPh}-(κ^2-L_4)(CO)(PPh_3)$_2$] (**6**). Selected bond lengths (Å) and angles (deg): Ru1−C1 = 1.846(3), Ru1−C11 = 2.111(3), Ru1−N1 = 2.168(2), Ru1−P1 = 2.3784(7), Ru1−P2 = 2.4222(7), Ru1−S1 = 2.4609(7), S1−C2 = 1.687(3), C11−C12 = 1.362(3), C19−C20 = 1.199(3); P1−Ru1−P2 = 179.40(2), C1−Ru1−C11 = 87.27(10), C1−Ru1−N1 = 100.13(10), C1−Ru1−P1 = 94.92(8), C11−Ru1−P1 = 86.56-(7), N1−Ru1−P1 = 92.16(6), C1−Ru1−P2 = 85.30(8), C11−Ru1−P2 = 92.90(7), N1−Ru1−P2 = 88.35(6), C11−Ru1−S1 = 92.55(7), P1−Ru1−S1 = 87.88(2), P2−Ru1−S1 = 91.90(2), N1−Ru1−S1 = 80.09(6), C12−C11−Ru1 = 124.74-(19).

(PPh_3)$_2$], in which the lability of the BTD ligand in solution provides a vacant site for alkyne coordination, leading to subsequent hydrometalation.[36] The complex [Os(CH=CH_2)Cl(BTD)(CO)(PPh_3)$_2$] reacted with **HL_4** to give a deep red complex which displayed a new carbonyl-associated absorption at 1892 cm^{-1} in the solid-state infrared spectrum. The product also showed characteristic resonances for the ethenyl and **L_4** ligands in the ^{1}H NMR spectrum and was formulated as [Os(CH=CH_2)(κ^2-L_4)(CO)(PPh_3)$_2$] (**7**).

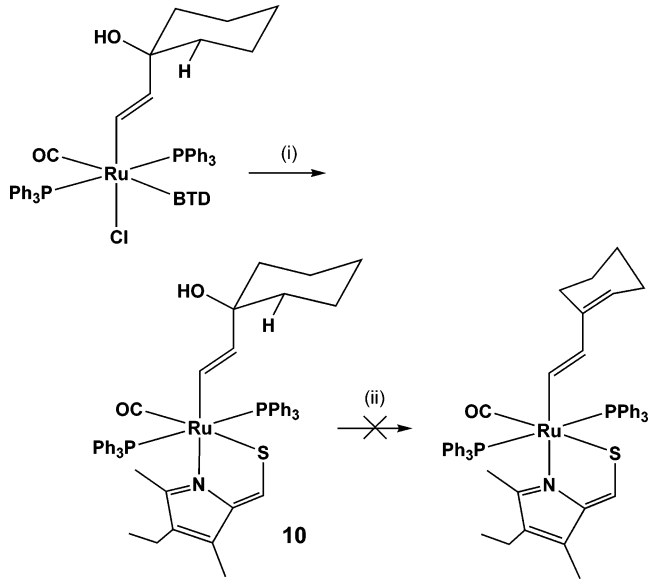
Dehydration Reactions. The complex [RuHCl(CO)-(BTD)(PPh_3)$_2$] readily hydroruthenates 1,1′-diphenylpropyn-1-ol to yield the γ-hydroxyalkenyl complex [Ru-(CH=CHCPh_2OH)Cl(CO)(BTD)(PPh_3)$_2$] in a reaction directly analogous to that for the corresponding BSD (2,1,3-benzoselenadiazole) complex.[29] On treatment with **HL_4** in the presence of sodium methoxide, the chloride and BTD ligands are displaced to provide the pale orange complex [Ru(CH=CHCPh_2OH)(κ^2-L_4)(CO)(PPh_3)$_2$] (**8**) in good yield. In addition to the resonances for the **L_4** ligand, a singlet at 1.60 ppm was assigned to the hydroxy group in the ^{1}H NMR spectrum. Treatment of **8** with tetrafluoroboric acid−diethyl ether complex led to an immediate color change to deep red. The reaction was carried out as a suspension in diethyl ether to avoid further reaction of the organometallic species with the acid. The product displayed a very low field doublet of triplets resonance at 16.03 ppm (J_{HH} = 14.1, J_{HP} = 2.5 Hz) and a doublet at 8.40 ppm (J_{HH} = 14.1 Hz) in the ^{1}H NMR spectrum. The features associated with the **L_4** ligand were retained, as were those for the phenyl substituents of the alkenyl ligand. The ν(CO) absorption in the solid-state infrared spectrum was observed at

Scheme 5[a]



[a] Legend: (i) HBF_4·OEt_2.

Scheme 6[a]



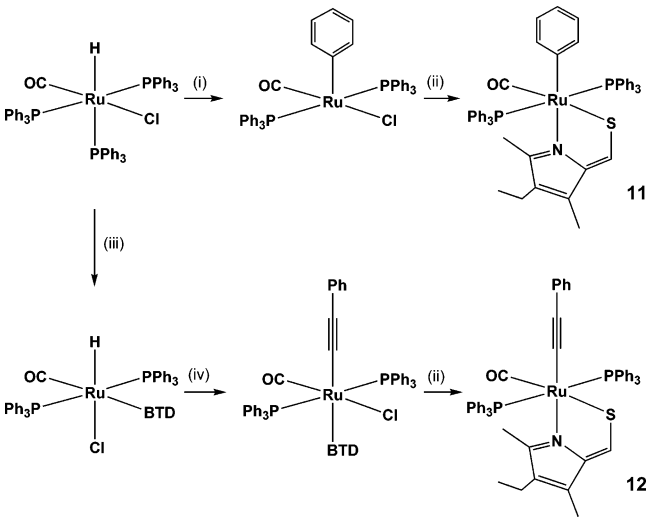
[a] Legend: (i) **HL_4**, NaOMe; (ii) base.

1971 cm^{-1} (blue shifted by 48 cm^{-1} from 1923 cm^{-1} in the precursor, **8**) indicating a decrease in electron density at the metal and consistent with formation of a cationic complex. A broad ν(B−F) band observed at 1055 cm^{-1} was attributed to a BF_4^- counteranion, and a new feature at 1568 cm^{-1} was assigned as a ν(Ru=CC=C) band. On the basis of these and mass spectrometry data, the product was formulated as the vinylcarbene complex [Ru(=CHCH=CPh_2)(κ^2-L_4)(CO)(PPh_3)$_2$]BF_4 (**9**) (Scheme 5). These data compare well to those for the complex [$RuCl_2$(=CHCH=CPh_2)(PPh_3)$_2$] reported by Grubbs.[41]

Hill and co-workers reported that the propargylic alkenyl complex [Ru{CH=CH(HO)C_6H_{10}}Cl(CO)(BSD)-(PPh_3)$_2$] was formed from the hydrometalation of ethynyl-1-cyclohexanol by [RuHCl(CO)(BSD)(PPh_3)$_2$].[33] The BTD analogue of this alkenyl compound was found to react with **HL_4** and sodium methoxide to give [Ru-{CH=CH(HO)C_6H_{10}}(κ^2-L_4)(CO)(PPh_3)$_2$] (**10**) (Scheme 6). Evidence for the retention of the alkenyl ligand was provided by two doublet of triplets resonances in the ^{1}H NMR spectrum for the α- and β-protons at 7.36 (J_{HH} = 17.2, J_{PH} = 2.5 Hz) and 5.4 (J_{HH} = 17.2 Hz, J_{HP} = 2.0 Hz) ppm, respectively. A resonance at 1.26 ppm observed among the cyclohexyl resonances (1.17−1.37 ppm) was attributed to the hydroxy group. A molecular ion was not seen in the FAB mass spectrum, only a peak

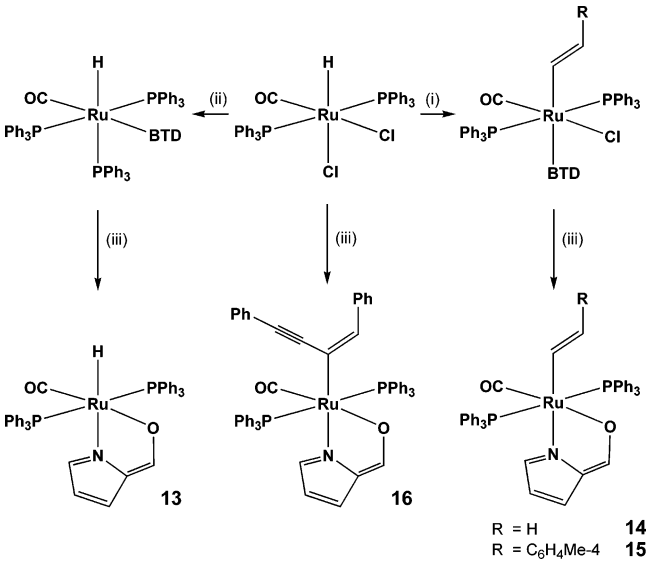
(41) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974.

Scheme 7[a]



[a] Legend: (i) $HgPh_2$; (ii) **HL_4**, NaOMe; (iii) BTD (2,1,3-benzothiadiazole); (iv) $Hg(C{\equiv}CPh)_2$.

Scheme 8[a]



[a] Legend: (i) HC≡CR (R = H, C_6H_4Me-4); (ii) BTD (2,1,3-benzothiadiazole); (iii) **HL_6**, NaOMe.

at *m/z* 928 corresponding to loss of water. We have recently discovered that $[Ru\{CH{=}CH(HO)C_6H_{10}\}Cl(CO)(BTD)(PPh_3)_2]$ is dehydrated in the course of the reaction with 1-methylimidazolethiolate (MI) and base to give the cyclohexenylalkenyl species $[Ru(CH{=}CHC_6H_9)(\kappa^2\text{-MI})(CO)(PPh_3)_2]$,[42] which displays a triplet resonance for the olefinic proton at 4.79 (J_{HH} = 3.5 Hz) ppm. This was not observed in the ^{1}H NMR spectrum of **10**. Attempts to form the complex $[Ru(CH{=}CHC_6H_9)(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$ by treatment of **10** with base (NaOMe, KOH, trifluoroacetic anhydride) failed to yield the desired product, and treatment with $HBF_4{\cdot}OEt_2$ led to cleavage of the alkenyl ligand.

Aryl and Alkynyl Complexes. The study was extended to include complexes bearing other σ-organyl ligands. The **HL_4** ligand reacted with the versatile 16-electron aryl complex $[Ru(C_6H_5)Cl(CO)(PPh_3)_2]$ reported by Roper[34] to occupy the vacant site and replace the chloride ligand to yield $[Ru(C_6H_5)(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$ (**11**) (Scheme 7). A molecular ion at *m/z* 895 and elemental analysis of the dichloromethane solvate confirmed the overall formulation.

Bis(alkynyl)mercurials can be used to prepare alkynyl complexes of the form $[M(C{\equiv}CR)Cl(CO)(L)(PPh_3)_2]$ (M = Ru,[32] Os;[35] L = BSD,[32] BTD[35]) from $[MHCl(CO)(L)(PPh_3)_2]$. An example of a complex bearing both **L_4** and alkynyl ligands, $[Ru(C{\equiv}CR)(\kappa^2\text{-}L_4)(CO)(PPh_3)_2]$ (**12**), was prepared from $[Ru(C{\equiv}CR)Cl(CO)(BTD)(PPh_3)_2]$ and HL_4 with base. The presence of the alkynyl ligand in the product was shown by the characteristic $\nu(C{\equiv}C)$ absorption in the solid-state infrared spectrum at 2097 cm^{-1}. Mass spectrometry and elemental analysis data were in good agreement with the above formulation.

Pyrrolecarboxaldehyde Complexes. In contrast to the pyrrolecarbothioaldehyde complexes prepared in this study, the corresponding oxygen analogue, pyrrole-2-carboxaldehyde (HL_6), is available commercially and has been used in the chelation of Zn(II), Cu(II), Ni(II), and Fe(III) ions[43] and as the precursor to pyrollide imine ligands used in ethylene polymerization precatalysts.[44] As no ruthenium complexes with this ligand have been reported to the best of our knowledge, a series of ruthenium hydride and alkenyl complexes was prepared. The absence of substitution on the pyrrole ring is unlikely to play a significant role in the steric profile of the ligand, allowing comparisons to the coordinated **L_4** ligand to be made directly.

The oxygen analogue of complex **1** was prepared by reaction of $[RuHCl(BTD)(CO)(PPh_3)_2]$ with HL_6 and sodium methoxide (Scheme 8). The yellow crystalline product $[RuH(\kappa^2\text{-}L_6)(CO)(PPh_3)_2]$ (**13**) gave rise to a strong ν(CO)-associated absorption in the solid-state infrared spectrum at 1925 cm^{-1} and a band of medium intensity attributed to $\nu(C{=}O)$ for the L_6 ligand at 1563 cm^{-1}. This frequency is much lower than that reported for the same feature in the free ligand (1668 cm^{-1}).[45] As for complex **1**, no ν(Ru−H) absorption was seen, due to overlap with the broad carbonyl band. However, the presence of the hydride ligand was confirmed by a triplet (J_{PH} = 20.5 Hz) in the ^{1}H NMR spectrum at −9.99 ppm. In addition to this high-field feature and those of the aromatic protons, four resonances corresponding to the pyrrolecarboxaldehyde ligand were observed in the ^{1}H NMR spectrum of complex **13**. A doublet of doublets was observed at 6.02 ppm (J_{HH} = 4.1, J_{HH} = 1.2 Hz), a doublet at 6.53 ppm (J_{HH} = 4.1 Hz), a broad singlet at 6.80 ppm, and a pseudo-quartet at 7.55 ppm ($J_{HH} \approx J_{HP}$ = 1.3 Hz). On the basis of its low-field chemical shift and later 2D-NMR experiments for complex **15**, this resonance was assigned to the CHO proton. In a homodecoupling ^{1}H NMR experiment, the resonance at 6.02 ppm was decoupled, causing the resonances at 6.53 and 6.80 ppm to become sharp singlets, while that for the CHO proton at 7.55 ppm was unaffected. This evidence indicated that the irradiated proton must be H^4 (numbering scheme in Chart 3). A

(42) Wilton-Ely, J. D. E. T.; Honarkhah, S. J.; Wang, M.; Tocher, D. A.; Slawin, A. M. Z. Unpublished results.

(43) Perry, C. L.; Weber, J. H. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1031.

(44) Bellabarba, R. M.; Gomes, P. T.; Pascu, S. I. *Dalton* **2003**, 4431. Chakravorty, A.; Holm, R. H. *Inorg. Chem.* **1964**, *3*, 1521.

(45) SBDS Integrated Spectral Data Base System for Organic Compounds,; National Institute of Advanced Industrial Science and Technology, of Japan, www.aist.go.jp/RIODB/SDBS/menu-e.html.

selective nuclear Overhauser enhancement (NOE) experiment, centered on the peak at 7.55 ppm, resulted in an enhancement of only the resonance at 6.53 ppm. This confirmed that the resonance at 6.53 ppm was due to the proton closest to the CHO proton: i.e., H^3. The remaining proton at 6.80 ppm was assigned as H^5. These assignments were supported by those for the free ligand in the literature (6.34 (H^4), 7.01 (H^3), 7.19 (H^5) and 9.50 ppm (CHO)),[45] which are all shifted to higher field on coordination to the metal. The resonance for the CHO proton is shifted to the greatest degree (by 1.95 ppm), indicating the significant shielding effect of the ruthenium center. The same effect is noted for the CSH proton in the complexes of the $\mathbf{HL_4}$ ligand.

The parent alkenyl complex [Ru(CH=CH_2)(κ^2-L_6)(CO)(PPh_3)$_2$] (**14**) was prepared from [Ru(CH=CH_2)Cl(CO)(PPh_3)$_2$] with HL_6 and sodium methoxide. The NMR spectral data for the ethenyl ligand were similar to those observed in complexes **2** and **7**. Additionally, four resonances with chemical shift values almost identical with those for complex **13** were observed for the $\mathbf{L_6}$ ligand. The $^{13}C\{^1H\}$ NMR spectrum consisted of four resonances for the carbons of the pyrrole ring at 116.8 (C^4), 122.7 (C^3), 144.7 (C^2), and 146.5 ppm (C^5) and another for the CHO carbon at 177.6 ppm. These were assigned initially on the basis of the literature data for the free ligand (C^4, 111.3 ppm; C^3, 122.1 ppm; C^2, 132.9 ppm; C^5, 127.3 ppm; CHO, 179.5 ppm)[45] and later confirmed by two-dimensional NMR experiments (HMQC, HMBC). Of the pyrrole ring protons, the greatest change with respect to the free ligand is observed in the chemical shifts of the C^2 and C^5 resonances, which are shifted to higher field. This is to be expected, as these carbons are bonded directly to the coordinated nitrogen. Perhaps surprisingly, the CHO resonance shows little change, especially when compared to the large upfield shift displayed by the CSH carbon in the $\mathbf{L_4}$ ligand on coordination to the metal. An HMQC NMR experiment was used to correlate the alkenyl and pyrrole protons with the respective carbon resonances in the $^{13}C\{^1H\}$ NMR spectrum. The lowest field carbon resonance at 208.7 ppm was assigned to the carbonyl ligand and showed coupling to the two mutually trans phosphines of 15.5 Hz. It is also noteworthy that both alkenyl carbon resonances displayed coupling to the phosphorus nuclei; however, this was only resolved fully for the α-carbon. The monosubstituted and disubstituted alkenyl derivatives [Ru(CH=$CHC_6H_4CH_3$-4)(κ^2-L_6)(CO)(PPh_3)$_2$] (**15**) and [Ru{C(C≡CPh)=CHPh}(κ^2-L_6)(CO)(PPh_3)$_2$] (**16**) were prepared from the precursors [Ru(CH=$CHC_6H_4CH_3$-4)Cl(CO)(BTD)(PPh_3)$_2$] and [Ru{C-(C≡CPh)=CHPh}Cl(CO)(PPh_3)$_2$], respectively, by reaction with $\mathbf{HL_6}$ and NaOMe. Spectroscopic data were found to be similar to those for the other $\mathbf{L_6}$ derivatives and fully supported the formulation given here. Complex **15** was obtained as a highly crystalline solid, and single crystals suitable for X-ray diffraction were grown from a dichloromethane−ethanol mixture. The crystal structure is shown in Figure 4.

The osmium analogue of complex **14**, [Os(CH=CH_2)(κ^2-L_6)(CO)(PPh_3)$_2$] (**17**), was prepared from [Os(CH=CH_2)Cl(CO)(BTD)(PPh_3)$_2$] and $\mathbf{HL_6}$ with NaOMe. As expected, the ν(CO) absorption in the solid-state infrared spectrum at 1896 cm^{-1} reflects the greater electron density of the osmium center compared to that in the ruthenium complex (ν(CO) 1946 cm^{-1}). Otherwise, the spectroscopic data were found to be similar to those for the other complexes bearing the $\mathbf{L_6}$ ligand.

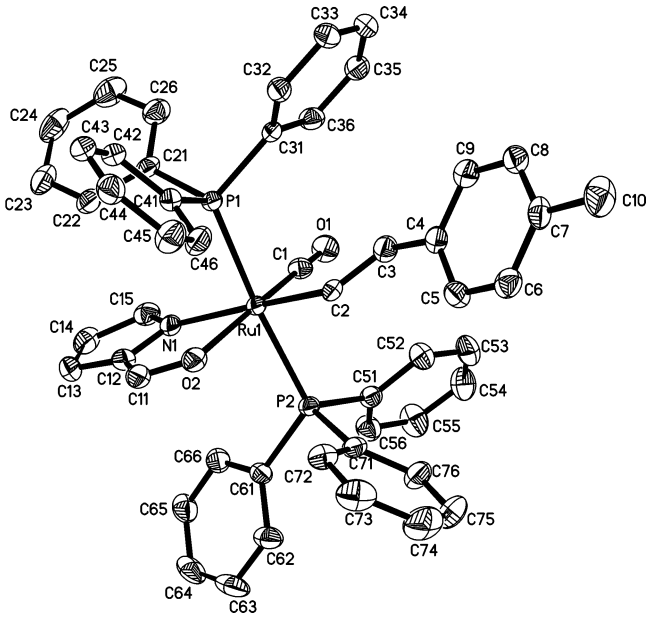


Figure 4. Molecular structure of [Ru(CH=$CHC_6H_5CH_3$-4)(κ^2-L_6)(CO)(PPh_3)$_2$] (**15**). Selected bond lengths (Å) and angles (deg): Ru1−C1 = 1.828(4), Ru1−C2 = 2.067(3), Ru1−N1 = 2.146(3), Ru1−O2 = 2.154(3), Ru1−P2 = 2.3785(9), Ru1−P1 = 2.3947(9), O2−C11 = 1.274(5), C2−C3 = 1.325(5); C1−Ru1−C2 = 94.34(15), C1−Ru1−N1 = 96.73(15), C2−Ru1−O2 = 92.17(12), C1−Ru1−P2 = 90.37(12), C2−Ru1−P2 = 85.33(10), N1−Ru1−P2 = 96.88(8), O2−Ru1−P2 = 87.00(7), C1−Ru1−P1 = 92.97(12), C2−Ru1−P1 = 85.61(10), N1−Ru1−P1 = 91.50(8), O2−Ru1−P1 = 90.68(7), P2−Ru1−P1 = 170.56(3), N1−Ru1−O2 = 76.92(12), C3−C2−Ru1 = 133.8(3).

Structural Discussion

The structure of the ligand 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde ($\mathbf{HL_4}$) was determined by single-crystal X-ray diffraction (Figure 1). This revealed the molecules to be planar, with only the methyl substituent of the ethyl group out of the plane. As shown in Chart 2, thioaldehyde and thiolate resonance forms are possible. In the structure of $\mathbf{HL_4}$, the bond lengths of the pyrrole ring suggest the thiolate form with the C1−C2 (1.382(3) Å) and C3−C4 (1.396(3) Å) distances slightly shorter than the C2−C3 (1.413(3) Å) and C4−C5 (1.407(3) Å) distances. However, the similarity in the bond lengths between carbons C2, C3, C4, and C5 indicates that the contribution from the thioaldehyde form is also significant. This is supported by the detection of the pyrrole (H^1) proton, which was located from a difference map and refined isotropically without constraints. However, the distance C5−N1 (1.342(3) Å) is significantly shorter than that for C2−N1 (1.388(3) Å), as would be expected for the thiolate form, and the C1−S1 distance of 1.658(3) Å is accordingly longer than literature values for C=S double bonds,[46] though this could be due to its

(46) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1.

Table 2. Selected Bond Data for Divalent Ruthenium Alkenyl Complexes[a]

complex	Ru−Cα	Cα−Cβ	Ru−Cα−Cβ	Cα−Cβ−Cγ
[Ru(CH=CH_2)(κ^2-L_4)(CO)L_2] (**2**)	2.083(2)	1.330(3)	131.31(19)	
[Ru{C(C≡CPh)=CHPh}(κ^2-L_4)(CO)L_2] (**6**)	2.111(3)	1.362(3)	124.74(19)	131.4(2)
[Ru(CH=CHC_6H_4R-4)(κ^2-L_6)(CO)L_2] (**15**)	2.067(3)	1.325(5)	125.2(4)	125.2(4)
[Ru(CPh=CHPh)Cl(CO)L_2][16]	2.03(1)	1.37(2)	130.7(9)	125(1)
[Ru(CH=CH_2)(CO)([9]aneS_3)L]$^+$ [23]	2.097(5)	1.292(7)	130.3(5)	
[Ru(CH=CH_2){κ^2-$H_2B(pz)_2$}(CO)L_2][22c]	2.080(7)	1.345(11)	131.1(6)	
[Ru{C(CO_2R)=CHCO_2R}(CO)(NCR)$_2L_2$]$^+$ [19f]	2.12(5)	1.54(7)	122(4)	127(5)
[Ru(CH=CHC_3H_7)Cl(CO)(MeHpz)L_2][52]	2.05(1)	1.32(2)	134(1)	126(1)
[Ru(CH=CHPh)(κ^2-O_2CR)(CO)L_2][24d]	2.030(15)	1.294(14)	125.6(8)	126.8(6)
[Ru(CH=CHPh)(κ^2-O_2CH)(CO)L_2][24a]	2.036(8)	1.35(1)	124.4(7)	123.4(1)

[a] Distances are given in Å and angles in deg; L = PPh_3; R = Me.

participation in internuclear hydrogen-bonding interactions. Such contacts were found to be present but very long (average of 2.82 Å) and therefore are not discussed in detail here. A pyrrolecarbothioaldehyde compound, 3-(2-(methoxycarbonyl)ethyl)-4-((methoxycarbonyl)-methyl)-5-methyl-2-(thioformyl)pyrrole, prepared from the corresponding aldehyde using Lawesson's reagent, was structurally characterized by Battersby and coworkers.[47] The bond distances and angles in this structure are generally similar to those in the structure of **HL_4**, apart from the distance corresponding to C1−C2, which is slightly longer in the literature complex (1.400 Å).

All of the structures of the metal complexes discussed here are of distorted-octahedral geometry. The interligand angles in the structure of [Ru(CH=CH_2)(κ^2-L_4)-(CO)$(PPh_3)_2$] (**2**) fall in the range 80.20(5)−96.72(8)°. The greatest deviation from 90° in all three structurally characterized complexes is due to the small bite angle of the **L_4** (or **L_6**) ligand, which is 80.20° in the structure of **2**. This is significantly smaller than the bite angles (83.3(6)−85.3(4)°) found in derivatives of the bidentate purinethione (pt) ligand in complexes such as [Ru(κ^2-pt)$_2(PPh_3)_2]^{2+}$,[48a,b] [$RuCl_2$(κ^2-pt)$(SbPh_3)_2$],[48c] and [Ru(κ^2-pt)$(bpy)_2]^{2+}$ (bpy = 2,2′-bipyridine).[48d] These purinethione ligands also form five-membered rings through nitrogen and sulfur donors (like **L_4**) but donate four electrons to the metal center (as opposed to three from **L_4**). The C−S bond length in such ligands (1.669(16) − 1.674(5) Å) is close to that of 1.679 Å in free purine-6-thione, indicating no substantial change in the C=S double bond on coordination of the purinethione ligand. A comparison of the bond lengths of the coordinated **L_4** ligand in **2** reveal that the C2−C3, C4−C5, and C6−N1 bond lengths of 1.368(3), 1.367(3), and 1.337(3) Å are significantly shorter than the C3−C4, C5−C6, and C3−N1 lengths of 1.432(3), 1.439(3), and 1.403(3) Å. The C3−C4, C5−C6, and C2−N1 distances are all longer than the corresponding distances in the structure of the free ligand **HL_4**, while the lengths of C2−C3 and C4−C5 decrease and C6−N1 remains the same. These data show that, on coordination, the ligand structure more closely resembles the thiolate form. A similar situation is found in the palladium complex [Pd(η^2(*C,N*)-$C_6H_4CH_2NMe_2$)(κ^2-**L_4**)], prepared as part of this research program.[49] In contrast to the purinethione complexes mentioned above, the C−S distance of 1.658(3) Å in **HL_4** changes significantly on coordination to the ruthenium center in complex **2**, showing an increase in length to 1.706(2) Å. This bond length is considerably shorter than the C−S distance of 1.781(8) Å in the thiolate complex [Ru(η^5-C_5H_5)(SPh)(dippe)]BPh_4[50] but longer than the C−S distance of 1.615(9) Å in the thioaldehyde complex [Ru(η^5-C_5H_5){S=CH(C_6H_4Cl-4)}(dppm)]PF_6,[51] indicating that a substantial degree of double-bond character remains. The bond lengths for the **L_4** ligand in [Ru{C(C≡CPh)=CHPh}(κ^2-**L_4**)(CO)$(PPh_3)_2$] (**6**) are effectively the same as for complex **2**. Complex **6** has interligand angles in the range 80.09(6)−100.13(10)°, and the data pertaining to the enynyl ligand are discussed in the context of the other alkenyl complexes in Table 2. As there is no direct precedent for the coordinated **L_4** ligand in the literature, it is useful to compare the structural data with those for [Ru(CH=$CHC_6H_5CH_3$-4)(κ^2-L_6)(CO)$(PPh_3)_2$] (**15**), which was also structurally characterized as part of this study. The interligand angles for **15** (76.92(12)−96.88(8)°) are in the same range as those for the other complexes with distorted-octahedral geometry. Examination of the **L_6** ligand reveals a number of differences from the **L_4** ligand. The C5−C6 distance of 1.439(3) Å for the **L_4** ligand in **2** is substantially longer than the corresponding **L_6** bond length of 1.401(6) Å in **15**, while the C3−C4 bond distance (in the **L_4** unit) of 1.432(3) Å (**2**) is shorter than that of 1.481(5) Å (C12−C13) in the **L_6** ligand in **15**. Overall, confident assignment of single and double bonds in the **L_6** ligand is not possible, as the bond lengths appear to be averaged throughout the ligand. The C11−O2 bond length of 1.274(5) Å falls between literature values for C−O (1.43 Å) and C=O (1.20 Å) bonds.[46]

Of the two **L_4** alkenyl complexes reported here, the Ru−Cα bond distance is shortest for the ethenyl complex **2**; however, this distance is longer than that in the **L_6** complex **15**, which is among the shortest of the representative alkenyl complexes collected in Table 2. The Cα−Cβ bond lengths for **2**, **6**, and **15** are unremarkable and fall in the typical range of alkenyl bond lengths.[13,52] The triple-bond length in the enynyl ligand

(47) Hawker, C. J.; Stark, W. M.; Spivey, A. C.; Raithby, P. R.; Leeper, F. J.; Battersby, A. R. *J. Chem. Soc., Perkin Trans 1* **1998**, 1493.

(48) (a) Cini, R.; Cinquantini, A.; Sabat, M.; Marzilli, L. G. *Inorg. Chem.* **1985**, *24*, 3903. (b) Cini, R.; Bozzi, R.; Karaulov, A.; Hursthouse, M. B.; Calafat, A. M.; Marzilli, L. G. *Chem. Commun.* **1993**, 899. (c) Bellucci, C.; Cini, R. *J. Inorg. Biochem.* **1999**, *76*, 243. (d) Yamanari, K.; Nozaki, T.; Fuyuhiro, A.; Kaizaki, S. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 109.

(49) Pogorzelec, P. J.; Reid, D. H.; Tocher, D. A.; Wilton-Ely, J. D. E. T. *Z. Naturforsch.* **2004**, *59b*, 1372.

(50) Coto, A.; de los Ríos, I.; Tenorio, M. J.; Puerta, C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1999**, 4309.

(51) Kuhnert, N.; Burzlaff, N.; Dombrowski, E.; Schenk, W. A. *Z. Naturforsch.* **2002**, *57b*, 259.

(52) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

in complex **6** is 1.199(3) Å and is similar to that found in free alkynes.[46]

The Ru−Cα−Cβ angle of 131.21(19)° in complex **2** shows much greater deviation from 120° than the corresponding angle in complexes **6** and **15** (Table 2). This is perhaps surprising, given the lower steric profile of the unsubstituted ethenyl ligand compared to the considerably bulkier mono- (**15**) and disubstituted (**2**) examples.

Concluding Remarks

A series of unusual carbothioaldehydes conjugated to pyrrole rings have been prepared and fully characterized by one- and two-dimensional NMR techniques and by X-ray crystallography. The coordination properties of a representative example as a nitrogen−sulfur mixed-donor ligand have been thoroughly studied with divalent ruthenium and osmium complexes bearing hydride, aryl, alkenyl, alkynyl, and carbene ligands. The coordination and structural properties of these species have also been compared with those bearing the nitrogen−oxygen mixed-donor analogue pyrrole-2-carboxaldehyde. This study provides a platform for further research on the effect of these mixed-donor chelates on the reactivity of coordinated organic ligands and their transformation.

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Supporting Information Available: CIF files giving crystallographic data for **HL_4**, **2**, **6**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050186G

(53) Torres, M. R.; Santos, A.; Perales, A.; Ros, J. *J. Organomet. Chem.* **1988**, *353*, 221.