# Multimetallic Arrays: Symmetrical and Unsymmetrical Bi-, Tri-, and Tetrametallic Organometallic Complexes of Ruthenium(II) and Osmium(II)

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Received July 20, 2008

The cationic complex  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]^+$  was prepared from the reaction of  $[Ru(C(\Xi CPh)=CHPh)Cl(CO)(BTD)(PPh_3)_2]$  (BTD = 2,1,3-benzothiadiazole) with the zwitterionic dithiocarbamate  $H_2NC_4H_8NCS_2$  and characterized structurally. In situ generation of the metalladithiocarbamate [ $Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NCS_2)(CO)(PPh_3)_2$ ] followed by treatment with  $[Ru(C(C = CPh) = CHPh)Cl(CO)(BTD)(PPh_3)_2]$  yielded the symmetrical bimetallic complex  $[{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2}_2(S_2CNC_4H_8NCS_2)]$ . The same product was also accessible by reaction of KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K with  $[Ru(C(C \equiv CPh) = CHPh)Cl(CO)(BTD)(PPh_3)_2]$ . This direct method also yielded the symmetrical bimetallic complexes [ $\{Ru(CH=CHR)(CO)(PPh_3)_2\}_2(S_2CNC_4H_8NCS_2)$ ] (R = Bu<sup>t</sup>, CPh<sub>2</sub>OH, C<sub>6</sub>H<sub>4</sub>Me-4, CO<sub>2</sub>Me, CH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>) and a tetrametallic species when  $R = C_5H_4FeC_5H_5$ . The osmium analogues  $[{Os(CR^1 = CHR^2)(CO)(PPh_3)_2}_2(S_2CNC_4H_8NCS_2)]$  (R<sup>1</sup> = C = CPh, R<sup>2</sup> = Ph; R<sup>1</sup> = H, R<sup>2</sup> = C<sub>6</sub>H<sub>4</sub>Me-4) were also prepared by this method. The stepwise deprotonation and functionalization of  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]^+$  with NEt<sub>3</sub> and CS<sub>2</sub> was utilized in the generation of the unsymmetrical complexes [{ $Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2$ }( $S_2CNC_4H_8NCS_2$ ){Ru(CH = CHR)- $(CO)(PPh_3)_2$  (R = Bu<sup>t</sup>, CPh<sub>2</sub>OH, C<sub>6</sub>H<sub>4</sub>Me-4, CO<sub>2</sub>Me, CH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>, C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>) and the heterobimetallic variant [{ $Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2$ }(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>){Os(CH = CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(P-1)(CO)(P  $Ph_{3}$ ]. The mixed carbonyl-thiocarbonyl complex [{ $Ru(C(\Xi CPh)=CHPh)(CO)(PPh_{3})_{2}$ }(S<sub>2</sub>CN- $C_4H_8NCS_2$  {Ru(C(C=CPh)=CHPh)(CS)(PPh\_3)\_2}] was also prepared by the same stepwise procedure. These are the first reported examples of alkenyl species bridged by a dithiocarbamate ligand. The similarly unprecedented linked bis(alkynyl)diruthenium complex [{ $Ru(C \equiv CBu^{t})(CO)(PPh_{3})_{2}$ }(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] was prepared by heating [{ $Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2$ }(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] with excess HC=CBu<sup>t</sup>. The first molecular complex bearing all three group 8 metals,  $[{Ru(C(C \equiv CPh) = CHPh)}]$ (CO)(PPh<sub>3</sub>)<sub>2</sub>{S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>{Os(CH=CHFc)(CO)(PPh<sub>3</sub>)<sub>2</sub>}], was achieved through the reaction of  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]^+$  with  $[Os(CH = CHFc)Cl(CO)(BTD)(PPh_3)_2]^ (Fc = C_5H_4FeC_5H_5, BTD = 2,1,3$ -benzothiadiazole). Further trimetallic species [{Ru(C(C= CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)}<sub>2</sub>M] (M = Ni, Pd, Pt, Zn) were prepared by the reaction of  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]^+$  with Ni(OAc)<sub>2</sub>, PdCl<sub>2</sub>(NCMe)<sub>2</sub>, PtCl<sub>2</sub>(NCPh)<sub>2</sub>, and  $Zn(OAc)_2$  in the presence of NEt<sub>3</sub> and CS<sub>2</sub>.

# Introduction

Many transition-metal dithiocarbamate complexes are known,<sup>1</sup> and a number of these have found use in applications as diverse as materials science, medicine, and agriculture. Their extensive metal-centered electrochemistry<sup>2</sup> and ability to stabilize a wide range of oxidation states have proved to be key factors in many applications. While polyfunctional variants of many ligands have been used to create multimetallic systems, this approach to dithiocarbamates has rarely been exploited.

Recent work to harness their versatility in the area of supramolecular design has illustrated their utility in this regard.<sup>3</sup> Our recent contributions in this area have centered on the use

of a piperazine dithiocarbamate that exists as a zwitterion.<sup>4</sup> This species can be used to coordinate to a first metal center, while retaining the potential to bond to a second on deprotonation and functionalization with  $CS_2$  at the other end. A general strategy for the synthesis of homo- and heterobimetallic

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CI

oc

. ₽Ph₃

F

Ph<sub>3</sub>P'S N R R N S PPh<sub>3</sub> E

complexes using a piperazine dithiocarbamate ligand is shown in Scheme 1.

A particularly intriguing aspect is the accessibility of heterobimetallic systems using this route. However, to date the metal units linked by such ligands<sup>5</sup> have been simple coordination compounds, largely neglecting the bridging of organotransition-metal centers. Few bimetallic ruthenium complexes with alkenyl ligands are known, and almost all are symmetrical in nature.<sup>6</sup> Some relevant examples of linked organometallics are shown in Scheme 2. Either the alkenyl ligand is utilized to bridge the metal centers (**A**, X = C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>, CH<sub>2</sub>C(OR)-

C(OR)CH<sub>2</sub>, (CH)<sub>2</sub>, (CH)<sub>4</sub>, (CH)<sub>6</sub>; **B**),<sup>7</sup> or the linker is a diamine (**C**), diisocyanide,<sup>7a</sup> or a bidentate dicarboxylate (**D**) unit.<sup>8</sup> Sulfur ligands are rarely used to link organometallic centers. An unusual example is that reported by Shaver,<sup>9</sup> in which a diruthenium complex (**E**) is isolated from the reaction of 2 equiv of [CpRu(PPh<sub>3</sub>)<sub>2</sub>SH] with *p*-phenylenediisothiocyanate while reaction of [RuHCl(CS)(PPh<sub>3</sub>)<sub>3</sub>] with 1,4-diethynylbenzene followed by treatment of carbon monoxide yields a bridging thioacyl (**F**).<sup>8</sup> Linked diosmium alkenyl complexes are extremely rare, with only two known examples derived from the double hydroosmiation of 1,3,5-triethynylbenzene.<sup>10</sup>

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None of these methods is widely applicable to the preparation of unsymmetrical heterobimetallic organometallic complexes. This report applies the approach outlined in Scheme 1<sup>4</sup> to the area of group 8 alkenyl chemistry.

#### **Results and Discussion**

A wide range of ruthenium alkenyl complexes<sup>11</sup> is readily accessible from hydrometalation of alkynes by the compounds [RuHCl(CO)L<sub>2/3</sub>] (L = P<sup>i</sup>Pr<sub>3</sub>,<sup>12</sup> PPh<sub>3</sub><sup>13</sup>), and many aspects of the resulting alkenyl complexes have been explored in fundamental work by the groups of Werner,<sup>14</sup> Esteruelas,<sup>15</sup> Santos,<sup>16</sup>

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Caulton,<sup>17</sup> Hill,<sup>18</sup> and others,<sup>19</sup> as well as by ourselves.<sup>20</sup> The most convenient triphenylphosphine-stabilized alkenvl complexes to use as starting materials are those of the forms [Ru(CR<sup>1</sup>=CHR<sup>2</sup>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>13</sup> and [Ru(CR<sup>1</sup>=CHR<sup>2</sup>)Cl(CO)- $(BTD)(PPh_3)_2$ ] (BTD = 2,1,3-benzothiadiazole),<sup>18a</sup> where BTD is a labile ligand. A marked advantage of the latter is that it avoids contamination with tris(phosphine) material. Reaction of [Ru(C(C=CPh)=CHPh)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] with the piperazine dithiocarbamate S2CNC4H8NH2 yielded the cation  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]Cl (1).$  The retention of the enynyl ligand was indicated by a broadened singlet resonance for  $H_{\beta}$  at 6.29 ppm in the <sup>1</sup>H NMR spectrum, while peaks for the piperazine protons were seen at 2.59 and 3.49 ppm. Resonances for the NH<sub>2</sub> protons were not generally observed and were assumed to be broad and/or obscured by other resonances. Three characteristic bands were visible in the solid-state infrared spectrum (KBr/Nujol) for the  $\nu_{C=C}$ ,  $\nu_{CO}$ , and  $\nu_{\rm CS}$  absorptions at 2148, 1924, and 999 cm<sup>-1</sup>, respectively. A mutually trans disposition of phosphines was indicated by a singlet in the <sup>31</sup>P NMR spectrum at 38.0 ppm. A molecular ion at m/z 1018 and satisfactory elemental analysis confirmed the overall composition of the compound. The particularly advantageous spectroscopic features of the enynyl ligand (H<sub> $\beta$ </sub> in <sup>1</sup>H NMR,  $\nu_{C=C}$  in IR) led to complex 1 being employed as the primary starting point for the multimetallic complexes described here. To complete the characterization of the compound, single crystals were grown and a structural study undertaken (Figure 1):

The geometry at the metal center is a slightly distorted octahedral arrangement with cis-interligand angles in the range 70.33(4)–93.16(14)°. The enynyl ligand is displaced by around 13° from the plane formed by the ruthenium center and the other donor atoms. Otherwise, the data associated with the enynyl ligand are comparable to those reported for previous examples.<sup>20a,b</sup> The S<sub>2</sub>CNC<sub>2</sub> unit of the dithiocarbamate ligand is almost coplanar, due to the well-established multiple-bond character of the C–N bond. The closest comparable structure is that of the bimetallic species [{(dppm)<sub>2</sub>Ru}<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)](BF<sub>4</sub>)<sub>2</sub>.<sup>4a</sup>

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Figure 1. Molecular structure of the cation in compound 1. Selected bond distances (Å) and angles (deg): Ru1-C1 = 1.831(5), Ru1-C12 = 2.109(5), Ru1-S2 = 2.466(1), Ru1-S1 = 2.508(1), O1-C1 = 1.166(6), S1-C2 = 1.707(5), S2-C2 = 1.697(6), N1-C2 = 1.354(7), C11-C12 = 1.351(7), C13-C14 = 1.215(7); S2-C2-S1 = 114.6(3), S2-Ru1-S1 = 70.33(4), C11-C12-Ru1 = 127.6(4), P1-Ru1-P2 = 173.73(4), C(13)-C(14)-C(15) = 169.9(6).

In both compounds the piperazine ring adopts a chair conformation. The Ru–S bond distances in compound **1** are slightly longer than those in the bimetallic examples, while the C–S and N–C distances are similar. However, the S2–Ru1–S1 angle of  $70.33(4)^{\circ}$  is smaller than that of  $71.40(7)^{\circ}$  in the previously reported complex.

Successive treatment of 1 with triethylamine, carbon disulfide, and [Ru(C(C=CPh)=CHPh)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] led to generation of the ammonium moiety and conversion into the bimetallic complex [{Ru(C(C=CPh)=CHPh)(CO)(PPh\_3)\_2}\_2(S\_2- $CNC_4H_8NCS_2$  (2), as shown in Scheme 3. The same product was obtained by reaction of the double salt KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K with 2 equiv of [Ru(C(C=CPh)=CHPh)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>]. As might be expected, compound 2 was found to display spectroscopic features similar to those of 1 with a broadened alkenyl resonance at 6.32 ppm and peaks between 2.21 and 2.27 ppm for the piperazine protons in the <sup>1</sup>H NMR spectrum, reflecting the different environments of the axial and equatorial protons. Integration of the aromatic region confirmed the presence of two Ru(PPh<sub>3</sub>)<sub>2</sub>(enynyl) units to one piperazine. Absorptions were observed in the solid-state infrared spectrum at 2153 ( $\nu_{C=C}$ ) and 1924 cm<sup>-1</sup> ( $\nu_{CO}$ ), further indicating retention of the enynyl and carbonyl ligands but failing to show any significant change from the same features in the precursor. A molecular ion in the FAB mass spectrum at m/z 1952 and good agreement of elemental analysis with the calculated values helped differentiate between compounds 1 and 2.

Initially, the reaction mixture to transform 1 into 2 was stirred for 2 h. However, the presence of side products was observed and these were attributed to insertion of carbon disulfide into the Ru–C bond, a reaction which has some precedent.<sup>21</sup> The reaction to form compound 2 is relatively rapid, and so best results were obtained using a method in which the reaction mixture was stirred only for 10 min before workup.

Further examples of symmetrical bimetallic species were prepared using the direct method outlined above. Reaction of 2 equiv of [Ru(CH=CHBu<sup>t</sup>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>led to the formation of NCS<sub>2</sub>K (Scheme 4)  $[{Ru(CH=CHBu^{t})(CO)(PPh_{3})_{2}}_{2}(S_{2}CNC_{4}H_{8}NCS_{2})]$  (3). A new carbonyl absorption was observed at 1908 cm<sup>-1</sup> in the solution infrared spectrum (CH<sub>2</sub>Cl<sub>2</sub>) and a new singlet in the <sup>31</sup>P NMR spectrum at 40.4 ppm. The retention of the alkenyl ligand was evidenced by a singlet at 0.02 ppm for the methyl protons in the <sup>1</sup>H NMR spectrum along with a doublet resonance for  $H_{\beta}$ at 5.95 ppm ( $J_{\rm HH} = 17.3$  Hz). The piperazine protons gave rise to a broad series of multiplets between 1.99 and 2.60 ppm. This dynamic behavior, presumably as a result of flexing of the piperazine ring, could not be frozen out at low temperatures (-40 °C) and coalesced to some extent at elevated temperatures (+40 °C). High-molecular-weight complexes often fail to yield a molecular ion in the mass spectrum, and this was found to be the case with complex 3: only fragmentations for loss of a alkenyl ligand and  $[M - alkenyl - PPh_3]^+$  were found at m/z1631 and 1367, respectively. The formulation was supported by elemental analysis, which was found to be in good agreement with calculated values. The complex [{ $Ru(CH=CHC_6H_4Me 4)(CO)(PPh_3)_2\}_2(S_2CNC_4H_8NCS_2)$  (4) was prepared in an identical manner.

Having prepared examples with both mono- and disubstituted alkenyl ligands, we decided to explore complexes with alkenyl moieties derived from propargyl alcohols (Scheme 4). The species [Ru(CH=CHCPh2OH)(BTD)Cl(CO)(PPh3)2] was obtained readily from the hydroruthenation of 1,1-diphenyl-2propyn-1-ol by [RuHCl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>]. This went on to react in a manner similar to that for complex 4 to yield a colorless product formulated as [{Ru(CH=CHCPh2OH)(CO)- $(PPh_3)_2$ <sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (5) on the basis of spectroscopic and analytical data. Treatment of [Ru(CH=CHCO2Me)-Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with 0.5 equiv of KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K yielded  $[{Ru(CH=CHCO_2Me)(CO)(PPh_3)_2}_2(S_2CNC_4H_8NCS_2)]$  (6). The ester group was seen as a medium-intensity  $\nu_{C=0}$  absorption at 1659 cm<sup>-1</sup>, to lower frequency of the more intense carbonyl absorption at 1917 cm<sup>-1</sup> in the solution (CH<sub>2</sub>Cl<sub>2</sub>) infrared spectrum. The methyl protons were observed at 3.37 ppm in the <sup>1</sup>H NMR spectrum along with  $H_{\alpha}$  and  $H_{\beta}$  at 9.47 ( $J_{HH} =$ 15.0 Hz) and 5.50 ppm, respectively.

In addition to the literature compounds employed, a number of new alkenyl complexes were prepared for use in the project. Reaction of HC=CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup> with [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] yielded a pale yellow product, formulated as the alkenyl complex [Ru(CH=CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (7). Singlet resonances in the <sup>1</sup>H NMR spectrum for the methyl and *tert*-butyl groups were observed at 0.15 and 0.78 ppm, respectively, along with a doublet for the methylene protons at 3.85 coupled to the H<sub>β</sub> proton ( $J_{HH} = 6.9$  Hz). A doublet of triplets of triplets was observed for H<sub>β</sub> at 4.82 ppm due to coupling with H<sub>β</sub>, the CH<sub>2</sub> protons, and the phosphine nuclei, while the resonance arising from H<sub>α</sub> appeared at 7.74 as a doublet of triplets.

The silyl-substituted alkenyl complex **7** reacts with KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K to give the off-white product [{Ru(CH= CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (**8**) in moderate yield (Scheme 4). The resonances for the alkenyl substituent proved particularly diagnostic, giving rise to singlets at -0.22 (SiCH<sub>3</sub>) and 0.77 ppm (Bu<sup>t</sup>) and a doublet at 3.44 ppm (CH<sub>2</sub>,  $J_{HH} = 5.8$  Hz).

In order to increase the number of metals incorporated into the system, ethynylferrocene was used to prepare the complexes

<sup>(21)</sup> Loumrhari, H.; Ros, J.; Yanez, R.; Torres, M. R. J. Organomet. Chem. 1991, 408, 233–239.





<sup>*a*</sup> Legend: (i)  $S_2CNC_4H_8NH_2$ ,  $NH_4BF_4$ ; (ii)  $NEt_3$ ,  $CS_2$ ,  $[Ru(C(C \equiv CPh) \equiv CHPh)Cl(CO)(BTD)(PPh_3)_2]$ ; (iii) 0.5 equiv of  $KS_2CNC_4H_8NCS_2K$ .

Scheme 4. Direct Preparation of Homobimetallic Ruthenium and Osmium Species<sup>a</sup>



<sup>a</sup> Legend: (i) 0.5 equiv of KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K; L = no ligand or BTD (2,1,3-benzothiadiazole).

[Ru(CH=CHFc)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**9**)<sup>22</sup> and [Os(CH=CHFc)Cl-(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (**10**) in good yield from reaction with [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] and [OsHCl(CO)(BTD(PPh<sub>3</sub>)<sub>2</sub>]. The presence of the ferrocenyl unit (in **9**) was clearly indicated by resonances at 3.78 (C<sub>5</sub>H<sub>5</sub>), 3.88 (C<sub>5</sub>H<sub>4</sub>), and 3.96 ppm (C<sub>5</sub>H<sub>4</sub>) in the <sup>1</sup>H NMR spectrum, while H<sub> $\alpha$ </sub> and H<sub> $\beta$ </sub> protons resonated as doublets (*J*<sub>HH</sub> = 13.3 Hz) at 7.74 and 5.39 ppm.

Use of [Ru(CH=CHFc)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] allows the introduction of a new carbon-bonded metal center into the system to create the tetrametallic product [{Ru(CH=CHFc)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>-(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (11) on reaction with KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (Scheme 4). Again, a multiplet was observed for the piperazine protons between 2.56 and 2.82 ppm in the <sup>1</sup>H NMR spectrum, while the ferrocenyl group gave rise to resonances slightly shifted with respect to those in the precursor. Resonances for H<sub>α</sub> and H<sub>β</sub> were observed at 7.70 and 5.84 ppm showing mutual coupling of 15.6 Hz. Somewhat surprisingly, a molecular ion was observed in the FAB mass spectrum at *m*/*z* 1967, albeit in low abundance.

While a number of linked bimetallic complexes of ruthenium are known (Scheme 2), very few examples have been reported for osmium. These are limited to the recently reported complexes  $[OsCl(CO)(PPh_3)_2(PR_3)](CH=CHC_6H_3(C=CH-3)CH=CH)-OsCl(CO)(PPh_3)_2(PR_3)]$  (R = Me, Ph) prepared by Jia and co-workers<sup>10</sup> and  $[OsCl(CO)(PPr_3)_2(CH=CH(CH_2)_4CH=CH)OsCl-(CO)(PPr_3)_2]$  by the group of Esteruelas.<sup>23</sup> Employing the versatile osmium starting materials [Os(alkenyl)Cl(CO)(BTD)- (PPh<sub>3</sub>)<sub>2</sub>] (alkenyl = CH=CHC<sub>6</sub>H<sub>4</sub>Me-4, C(C=CPh)=CHPh) in the reactions with KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K leads to the formation of the yellow products [{Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>-(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (**12**) and [{Os(C(C=CPh)=CHPh)(CO)-(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (**13**) in good to moderate yield (Scheme 4). Spectroscopic and analytical features were similar to those for the ruthenium analogues, with the exception of the resonances in the <sup>31</sup>P NMR spectrum at 8.3 (**12**) and 6.6 ppm (**13**), which displayed a shift to higher field due to the greater shielding afforded by the osmium centers. A molecular ion was observed at *m*/*z* 1957 in the FAB mass spectrum of **12**, and an excellent agreement with calculated values was found for the microanalytical data.

With the routes to symmetrical species well established, our attention turned to exploring the wider potential of this methodology to prepare unsymmetrical bimetallic species. Using the complex  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO) (PPh_3)_2$ ]Cl (1) as the starting point due to the characteristic features in its IR and <sup>1</sup>H NMR spectra, the addition of different alkenyl species was investigated. Treatment of 1 with triethylamine and carbon disulfide followed by addition of [Ru(CH= CHBu<sup>t</sup>)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] led to the formation of a yellowbrown product. Retention of the enynyl moiety was indicated by the  $\nu_{C=C}$  absorption at 2152 cm<sup>-1</sup> in the solid-state infrared spectrum and a singlet resonance in the <sup>1</sup>H NMR spectrum at 6.21 ppm. Only one broadened  $\nu_{CO}$  absorption was observed in the solution infrared spectrum (CH<sub>2</sub>Cl<sub>2</sub>) at 1912 cm<sup>-1</sup>, but additional peaks in the <sup>1</sup>H NMR spectrum at 0.34 (s, Bu<sup>t</sup>) and 4.54 ppm (d, CHBu<sup>t</sup>,  $J_{\rm HH} = 16.4$  Hz) indicated the presence of the new metal unit. This was corroborated by two distinct phosphorus environments in the <sup>31</sup>P NMR spectrum at 38.0 and

<sup>(22)</sup> Wilson, D. J. M.Sc. Thesis, Imperial College, 1996.

<sup>(23)</sup> Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Valero, C.; Zeier, B. J. Am. Chem. Soc. **1995**, 117, 7935–7942.

Scheme 5. Preparation of Unsymmetrical Bimetallic Ruthenium Species<sup>a</sup>



40.6 ppm. By comparison with the chemical shift of the starting material, these were assigned to the Ru(PPh<sub>3</sub>)<sub>2</sub> units bonded to the enynyl and tertiarybutyl alkenyl ligands, respectively. A fragment for loss of phosphine at m/z 1568 in the FAB mass spectrum and elemental analysis confirmed the overall formulationas[{Ru(C(C=CPh)=CHPh)(CO)(PPh\_3)<sub>2</sub>}(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>){Ru-(CH=CHR)(CO)(PPh\_3)<sub>2</sub>}] (R = Bu<sup>t</sup>, 14).

In a similar manner (Scheme 5), further examples of unsymmetrical bimetallics with units bearing monosubstituted alkenyl ligands ( $R = C_6H_4Me-4$  (15), CPh<sub>2</sub>OH (16), CO<sub>2</sub>Me (17),  $CH_2OSiMe_2Bu^t$  (18)) were prepared. These constitute the first examples of unsymmetrical organometallic complexes bridged by a dithiocarbamate linkage. Using [Ru(CH=  $CHFc)Cl(CO)(PPh_3)_2]$ (9), a trimetallic species, [{Ru(C(C=CPh)= CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>}(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>){Ru(CH=CHFc)(CO)(P- $Ph_{3}_{2}$  [19), was prepared from 1 in the same manner. In addition to the peak at 37.8 ppm in the <sup>31</sup>P NMR spectrum for the enynyl end of the molecule, a new resonance at 39.3 ppm was observed for the ferrocenyl alkenyl unit as well as typical resonances in the <sup>1</sup>H NMR spectrum, similar to those found in 9 and 11. The success of these reactions led to an attempt to introduce a different metal center as the new end unit. The BTD and chloride ligands in the complex [Os(CH=CHC6H4Me-4)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] were readily displaced by the metalladithiocarbamate  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NCS_2)$ -(CO)(PPh<sub>3</sub>)<sub>2</sub>][NHEt<sub>3</sub>], generated in situ, to yield the mixed-metal  $[{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2}(S_2CNC_4$ species  $H_8NCS_2$  {Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub> ] (20) in moderate yield. This complex joins the species [RuCl(CO)- $(PPr_{3}^{i})_{2}(CH=CH(CH_{2})_{4}CH=CH)OsCl(CO)(PPr_{3}^{i})_{2}]$  as one of very few known ruthenium-osmium bimetallic compounds bearing alkenyl ligands.<sup>24</sup> As expected, a substantial difference was observed in the chemical shift of the phosphorus nuclei attached to the ruthenium (38.0 ppm) and osmium (8.1 ppm) centers. Other spectroscopic features in the <sup>1</sup>H NMR spectrum were similar to those observed previously. A molecular ion was clearly identifiable in the FAB mass spectrum at m/z 1953 along with fragmentations due to loss of phosphine and a fragment attributed to  $[M - PPh_3 - alkenyl]^+$ . Elemental analysis further supported the above formulation.

These results opened up the exciting possibility of a complex being accessible in which all three metals of the group 8 triad

(24) Buil, M.; Esteruelas, M. A. Organometallics 1999, 18, 1798-1800.

Scheme 6. Preparation of the Heterotrimetallic Group 8 Metal Complex 21<sup>a</sup>



<sup>*a*</sup> Legend: (i) S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>, NH<sub>4</sub>BF<sub>4</sub>; (ii) NEt<sub>3</sub>, CS<sub>2</sub>, [Os(CH=CHFc)-Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>].

are represented. This was indeed achieved with the synthesis of  $[{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2}(S_2CNC_4H_8NCS_2)]O_{s-1}$  $(CH=CHFc)(CO)(PPh_3)_2$ ] (21) by the same route (Scheme 6). Again, a broadened carbonyl absorption with a distinct shoulder to lower frequency was observed in the solution IR spectrum at 1927 cm<sup>-1</sup> (different from that found for the starting material) alongside a  $\nu_{C=C}$  band at 2152 cm<sup>-1</sup> and a new resonance at 7.9 ppm in the <sup>31</sup>P NMR spectrum pointed to the successful incorporation of the osmium unit. Typical resonances for the enynyl and ferrocenyl alkenyl ligands confirmed their presence. A peak assigned to loss of phosphine was identified at m/z 1784 in the FAB mass spectrum. Elemental analysis was found to agree well with calculated values. Although the compound was found to be reasonably microcrystalline, no crystals of sufficient quality for a structural determination could be grown. Apart from some cluster examples,<sup>25a</sup> to the best of our knowledge, this FeRuOs species is only the second example of a complex containing all three metals of the triad after the complex trans- $[(FcC \equiv C)C_6H_3\{C \equiv CRuCl(dppm)_2\}\{C \equiv COsCl(dppm)_2] re$ ported by Long and co-workers.<sup>25b</sup> Very recently, Lang and coworkers have reported an elegant synthetic route to a heptametallic complex containing the group 8 triad along with Ti, Re, Pt, and Cu centers.<sup>25c</sup>

Although the anionic metalladithiocarbamate  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NCS_2) (CO)(PPh_3)_2]^-$  was always generated in situ in the experiments outlined here, this species can be characterized as the  $[HNEt_3]^+$  salt on addition of NEt<sub>3</sub> and CS<sub>2</sub> to a solution of compound **1** in dichloromethane followed by precipitation with diethyl ether. The anion gave rise to two piperazine environments in the <sup>1</sup>H NMR spectrum at 2.44 and 4.02 ppm along with a resonance for H<sub>β</sub> at 6.29 ppm. The <sup>31</sup>P NMR resonance at 37.8 ppm is little changed from that of the precursor **1**. On standing in solution for more than 1 h, formation of the symmetrical species **2** began to occur. This behavior has been noted for the zwitterion  $[Ru(S_2CNC_4H_8NCS_2)(dppm)_2].^4$ 

A subtle variation on the unsymmetrical systems described above is the preparation of a bimetallic complex in which only one coligand differs at each end. The thiocarbonyl analogues of the alkenyl starting materials employed here are readily accessible from hydroruthenation of [RuHCl(CS)(BTD)(PPh\_3)\_2] or [RuHCl(CS)(PPh\_3)\_3].<sup>8</sup> Accordingly, [Ru(C(C=CPh)=-CHPh)(S\_2CNC\_4H\_8NH\_2)(CS)(PPh\_3)\_2]Cl (**22**) was prepared from [Ru(C(C=CPh)=CHPh)Cl(CS)(PPh\_3)\_2] by the same method as that used for **1**. Spectroscopic features were essentially identical to those for **1** other than the  $\nu_{CS}$  absorption at 1246 cm<sup>-1</sup>.



<sup>*a*</sup> Legend: (i) NEt<sub>3</sub>, CS<sub>2</sub>, [Ru(C(C=CPh)=CHPh)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>].

Treatment of **22** with NEt<sub>3</sub> and CS<sub>2</sub> followed by addition of [Ru(C(C=CPh)=CHPh)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] resulted in the formation (Scheme 7) of [{Ru(C(C=CPh)=CHPh)(CO)-(PPh<sub>3</sub>)<sub>2</sub>}(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>){Ru(C(C=CPh)=CHPh)(CS)(PPh<sub>3</sub>)<sub>2</sub>}] (**23**). As may be expected, multinuclear NMR spectroscopic features for both ends of the molecule, though clearly broadened, were so similar as to render them indistinguishable. However, a shift of the  $\nu_{CS}$  absorption to 1259 cm<sup>-1</sup> and the presence of the  $\nu_{CO}$  band at 1920 cm<sup>-1</sup> attested to the success of the reaction. A very broad <sup>31</sup>P NMR resonance centered at 34.1 ppm was observed, while fragmentation for [M - PPh<sub>3</sub>]<sup>+</sup> at *m/z* 1702 and satisfactory elemental analysis supported the formulation as that above.

The examples above have illustrated the versatility of the piperazine dithiocarbamate linkage in the synthesis of diverse symmetrical and unsymmetrical organometallic compounds. The next challenge was to explore the ability of this ligand to support functional group transformations of the  $\sigma$ -bonded organic ligands. Treatment of the symmetrical tolyl-substituted alkenyl complex  $[{Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2}_2(S_2CNC_4H_8-$ NCS<sub>2</sub>)] (4) with an excess of HC $\equiv$ CBu<sup>t</sup> in refluxing toluene resulted in a tan product which displayed a  $v_{CO}$  absorption in the solid-state infrared spectrum at 1947 cm<sup>-1</sup> along with a completely new band at 2102 cm<sup>-1</sup> in the region typical of alkynyl  $\nu_{C=C}$  bands. In the <sup>1</sup>H NMR spectrum, no AB system was observed for a tolyl group or  $H_{\alpha}$  or  $H_{\beta}$  protons. Instead, a singlet integrating to 18 protons was observed at 0.94 ppm. The MALDI mass spectrum showed a peak at m/z 1706 corresponding to the molecular ion for the alkynyl complex  $[{Ru(C \equiv CBu^{t})(CO)(PPh_{3})_{2}}_{2}(S_{2}CNC_{4}H_{8}NCS_{2})]$  (24) along with further fragmentations from loss of carbonyl and phosphine ligands (Scheme 8). Two closely separated peaks were observed in the room temperature <sup>31</sup>P NMR spectrum at 38.9 and 39.3 ppm, indicating slightly different environments for the two metal units, which coalesced on warming.

An alternative route to trimetallic complexes was also explored using metal precursors of groups 10 and 12 (Scheme 9), which are well-known to form bis(dithiocarbamate) species. Sequential treatment of 2 equiv of [Ru(C(C)])CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1) with excess triethylamine and carbon disulfide followed by 1 equiv of  $Ni(OAc)_2$  led to a yellow product in low yield. As might be expected, the spectroscopic features for the desired complex  $[\{Ru(C(C = CPh) = CHPh)(S_2CNC_4H_8NCS_2)(CO)(PPh_3)_2\}_2Ni]$ (25) were found to be very similar to those of 1. IN comparison to the same feature in 1, a slight shift was observed for  $H_{\beta}$  in the <sup>1</sup>H NMR spectrum to 6.30 ppm and the piperazine protons were spread over a slightly greater range of chemical shifts.

Scheme 8. Preparation of a Bis(alkynyl)ruthenium Species  $(24)^{\alpha}$ 



<sup>*a*</sup> Legend: (i) excess HC $\equiv$ CBu<sup>t</sup>, heat; R = C<sub>6</sub>H<sub>4</sub>Me-4.

Attempts to record a potentially diagnostic <sup>13</sup>C NMR spectrum were defeated by persistent precipitation of the complex from high concentration solutions over the period of data accumulation, leading to a poor signal-to-noise ratio. The mass spectrum failed to provide a molecular ion, only exhibiting a fragmentation attributed to m/z 1691 for loss of two phosphines and a carbonyl ligand. However, elemental analysis was found to be in excellent agreement with calculated values. Trimetallic compounds of the heavier congeners of group 10 were also prepared from PdCl<sub>2</sub>(NCMe)<sub>2</sub> and PtCl<sub>2</sub>(NCPh)<sub>2</sub> to yield  $[\{Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NCS_2)(CO)(PPh_3)_2\}_2M] (M$ = Pd, 26; M = Pt, 27), respectively. Data for these complexes were found to be similar to those exhibited by 25. The RuZnRu  $[{Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NCS_2)(CO)}]$ complex  $(PPh_3)_2$ <sub>2</sub>Zn] (28) was synthesized in a similar manner from 1 with NEt<sub>3</sub>, CS<sub>2</sub>, and zinc acetate to provide a group 12 example. While a square-planar geometry around the d<sup>8</sup> group 10 metals in 25-27 is assumed, the Zn(II) (d<sup>10</sup>) center in 28 is likely to adopt a tetrahedral arrangement.

## Conclusion

The methodology described above illustrates how the piperazine dithiocarbamate system can be used to link a range of organometallic centers. The accessibility of unsymmetrical systems via this route is particularly significant, as this is often impossible to achieve using conventional bifunctional linkages. Furthermore, the robust nature of the bis(dithiocarbamate) linker has been illustrated by a successful functional group transformation performed on a bimetallic complex, converting a dialkenyl compound into one bearing alkynyl ligands. The tri- and tetrametallic species prepared further illustrate the flexibility of the approach, allowing metal units to function as the connecting moiety between ruthenium alkenyl complexes. The potential of this idea, illustrated here by four-coordinate group 10 and 12 metals, will now be explored using units based on d- and f-block metals capable of chelating a greater number of dithiocarbamate ligands in order to expand the geometrical possibilities of the linkage metal atom.

### **Experimental Section**

**General Comments.** All experiments were carried out under aerobic conditions, and the majority of the complexes appear to be indefinitely stable toward the atmosphere in solution or in the solid state. Solvents were used as received from commercial sources. The following complexes have been described elsewhere: [RuHCl(CO)(P-

Scheme 9. Preparation of Ru<sub>2</sub>M Heterotrimetallic Species<sup>a</sup>



<sup>a</sup> Legend: (i) NEt<sub>3</sub>, CS<sub>2</sub>; (ii) Ni(OAc)<sub>2</sub>, PdCl<sub>2</sub>(NCMe)<sub>2</sub>, PtCl<sub>2</sub>(NCPh)<sub>2</sub> or Zn(OAc)<sub>2</sub>; M = Ni (25), Pd (26), Pt (27), Zn (28).

Ph<sub>3</sub>)<sub>3</sub>],<sup>26</sup> [RuHCl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>],<sup>27</sup> [OsHCl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>],<sup>18h</sup>  $[RuHCl(CS)(PPh_3)_3],^{28} [Ru(CR^1 = CHR^2)Cl(CO)(PPh_3)_2] (R^1 = H, R^2 = Bu^{t,16h} CO_2Me^{16i} \text{ and } R^1 = C = CPh, R^2 = Ph^{18a,b},$  $[Ru(CR^1=CHR^2)Cl(CO)(BTD)(PPh_3)_2]$  (R<sup>1</sup> = H, R<sup>2</sup> = C<sub>6</sub>H<sub>4</sub>Me-4,  $CPh_2OH$ ),<sup>18c</sup> [Os(CR<sup>1</sup>=CHR<sup>2</sup>)Cl(CO)(BTD)(PPh\_3)<sub>2</sub>] (R<sup>1</sup> = H, R<sup>2</sup> =  $C_6H_4Me-4$ ;  $R^1 = C \equiv CPh$ ,  $R^2 = Ph$ ),<sup>18h</sup> [PdCl<sub>2</sub>(NCMe)<sub>2</sub>],<sup>29</sup> [PtCl<sub>2</sub>(NCPh)<sub>2</sub>],<sup>30</sup> [S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>],<sup>4,31</sup> and [KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K].<sup>32</sup> MALDI-MS and FAB-MS data were obtained using Micromass TofSpec and Autospec Q instruments, respectively. The FAB mass spectrum for 15 was obtained at the EPSRC National Mass Spectrometry Service Center, University of Wales Swansea. Infrared data were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrometer, KBr plates were used for solid-state IR spectroscopy, and characteristic phosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25 °C using Varian Mercury 300 or Varian Unity 500 (for complex 7) spectrometers in CDCl<sub>3</sub> unless otherwise indicated. All couplings are in hertz, and <sup>31</sup>P NMR spectra are proton-decoupled. Elemental analysis data were obtained from London Metropolitan University. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes. Samples were recrystallized from a mixture of dichloromethane and ethanol for elemental analysis. Solvates were confirmed by integration of the <sup>1</sup>H NMR spectrum.

[**Ru**(**C**(**C**=**CPh**)=**CHPh**)(**CO**)(**PPh**<sub>3</sub>)<sub>2</sub>(**S**<sub>2</sub>**CNC**<sub>4</sub>**H**<sub>8</sub>**NH**<sub>2</sub>)]**C**1 (1). The reagent [S<sub>2</sub>CNC<sub>4</sub>**H**<sub>8</sub>NH<sub>2</sub>] (220 mg, 1.356 mmol) was dissolved in methanol (20 cm<sup>3</sup>) and the complex [Ru(C(**C**=**CPh**)= CHPh)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (1000 mg, 1.121 mmol) was added in dichloromethane (60 cm<sup>3</sup>). After the mixture was stirred at room temperature for 3 h, the volatiles were removed. The crude product was dissolved in a small amount of dichloromethane, and ethanol (20 cm<sup>3</sup>) was added. Slow concentration under reduced pressure gave a yellow product, which was filtered off, washed with hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 820 mg (69%). The BTD analogue of the starting material can also be used to give a comparable yield of compound **1**. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2153 ( $\nu_{C=C}$ ), 1927 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2148 ( $\nu_{C=C}$ ), 1924 ( $\nu_{CO}$ ), 1592, 1311, 1267,

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(32) Tombeux, J.; van Poucke, L. C.; Eeckhaut, Z. Spectrochim. Acta 1972, 28A, 1943–1947. 1245, 1203, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.59 (s, 4 H, NC<sub>4</sub>H<sub>8</sub>N), 3.49 (s, 4 H, NC<sub>4</sub>H<sub>8</sub>N), 6.29 (s, 1 H, H<sub>β</sub>), 6.94–7.57 (m, 40 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  41.4–42.1 (m, NC<sub>4</sub>H<sub>8</sub>N), 102.1, 98.4 (s × 2, C=C), 124.5–140.77 (m, C<sub>6</sub>H<sub>5</sub>), 126.4 (s, =CH), 146.6 (s, RuC=), 197.3 (t, CO, J<sub>PC</sub> = 17.7 Hz), 207.7 (s, CS<sub>2</sub>) ppm. <sup>31</sup>P NMR:  $\delta$  38.0 (s, PPh<sub>3</sub>) ppm. MS (FAB): *m*/*z* (%) 1018 (18) [M]<sup>+</sup>, 857 (10) [M - S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>]<sup>+</sup>, 815 (20) [M - alkenyl]<sup>+</sup>, 728 (56) [M - CO - PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 66.0; H, 4.9; N, 2.6. Calcd for C<sub>58</sub>H<sub>51</sub>ClN<sub>2</sub>OP<sub>2</sub>RuS<sub>2</sub>: C, 66.1; H, 4.9; N, 2.7.

[{Ru(C(C=CPh)=CHPh)(CO)(PPh\_3)\_2}\_2(S\_2CNC\_4H\_8NCS\_2)] (2). (a) KS\_2CNC\_4H\_8NCS\_2K (35 mg, 0.111 mmol) was dissolved in MeOH (15 cm<sup>3</sup>) and water (2 cm<sup>3</sup>), and [Ru(C(C= CPh)=CHPh)Cl(CO)(PPh\_3)\_2] (200 mg, 0.224 mmol) was added in dichloromethane (25 cm<sup>3</sup>). After the mixture was stirred at room temperature for 20 min, the solvent volume was reduced by rotary evaporation. The pale yellow product was filtered off, washed with water (5 cm<sup>3</sup>), ethanol (10 cm<sup>3</sup>), and hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 170 mg (78%).

(b) [Ru(C(C=CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (100 mg, 0.095 mmol) was dissolved in dichloromethane (15 cm<sup>3</sup>) and treated with NEt $_3$  (5 drops, excess) and CS $_2$  (5 drops, excess) followed by a dichloromethane solution (10 cm<sup>3</sup>) of  $[Ru(C(C = CPh) = CHPh)Cl(CO)(PPh_3)_2]$  (85 mg, 0.095 mmol). After the mixture was stirred at room temperature for 20 min, the solvent volume was reduced by rotary evaporation. The pale yellow product was filtered off, washed with water (5 cm<sup>3</sup>), ethanol (10 cm<sup>3</sup>), and hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 135 mg (73%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2144 ( $\nu_{C=C}$ ), 1915 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2153 ( $\nu_{C=C}$ ), 1924 ( $\nu_{CO}$ ), 1591, 1277, 1212, 1161, 1000 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.21–2.27 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 6.32 (s, 2 H, H<sub>β</sub>), 6.51–7.48 (m, 80 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR:  $\delta$  38.3 (s, PPh<sub>3</sub>) ppm. MS (FAB): m/z (%) 1952 (2) [M]<sup>+</sup>, 1689 (1) [M – PPh<sub>3</sub>]<sup>+</sup>, 1485 (3) [M – PPh<sub>3</sub> – alkenyl]<sup>+</sup>. Anal. Found: C, 67.9; H, 4.6; N, 1.5. Calcd for C<sub>112</sub>H<sub>90</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub> • 0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 67.8; H, 4.6; N, 1.4.

 $[{Ru(CH=CHBu^{t})(CO)(PPh_{3})_{2}}_{2}(S_{2}CNC_{4}H_{8}NCS_{2})]$  (3). KS<sub>2</sub>-CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (20 mg, 0.064 mmol) was dissolved in MeOH (10 cm<sup>3</sup>), and the complex [Ru(CH=CHBu<sup>t</sup>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (100 mg, 0.129 mmol) was added in dichloromethane (15 cm<sup>3</sup>). After the mixture was stirred at room temperature for 20 min, all solvent was removed by rotary evaporation. The product was taken up in a small amount of dichloromethane and filtered through diatomaceous earth. Ethanol (15 cm<sup>3</sup>) was added, and a pale brown powder was obtained after concentration under reduced pressure. The product was filtered off, washed with ethanol (10 cm<sup>3</sup>) and hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 64 mg (58%). IR  $(CH_2Cl_2)$ : 1908 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 1911 ( $\nu_{CO}$ ), 1731, 1601, 1580, 1272, 1122, 1040, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.02 (s, 18 H, Bu<sup>t</sup>), 1.99–2.60 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 5.95 (d, 2 H, H<sub> $\beta$ </sub>, <sup>3</sup>J<sub>HH</sub> = 17.3 Hz), 6.92–7.34 (m, 60 H + 2 H,  $C_6H_5 + H_{\alpha}$ ) ppm. <sup>31</sup>P NMR:  $\delta$  40.4 (s, PPh<sub>3</sub>) ppm. MS (FAB): m/z (%) 1631 (1) [M - alkenyl]<sup>+</sup>,

1367 (2)  $[M - alkenyl - PPh_3]^+$ . Anal. Found: C, 64.7; H, 5.2; N, 1.8. Calcd for  $C_{92}H_{90}N_2O_2P_4Ru_2S_4$ : C, 64.6; H, 5.3; N, 1.6.

[{**Ru**(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (4). This compound was prepared as for the synthesis of **3** using KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (29 mg, 0.092 mmol) and [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (150 mg, 0.186 mmol) to provide a pale yellow powder. Yield: 98 mg (59%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1916 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 1919 ( $\nu_{CO}$ ), 1659, 1279, 1213, 1117, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. NMR <sup>1</sup>H:  $\delta$  2.21 (s, 6 H, CH<sub>3</sub>), 2.68 – 2.94 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 5.57 (d, 2 H, H<sub>β</sub>, <sup>3</sup>J<sub>HH</sub> = 15.9 Hz), 6.36, 6.80 ((AB)<sub>2</sub>, 8 H, C<sub>6</sub>H<sub>4</sub>, J<sub>AB</sub> = 7.9 Hz), 7.27 – 7.51 (m, 60 H, C<sub>6</sub>H<sub>5</sub>), 7.69 (d, 2 H, H<sub>α</sub>, <sup>3</sup>J<sub>HH</sub> = 16.0 Hz) ppm. <sup>31</sup>P NMR:  $\delta$  39.7 (s, PPh<sub>3</sub>) ppm. MS (MALDI): *m*/*z* (%) 1518 (1) [M – PPh<sub>3</sub>]<sup>+</sup>, 1374 (1) [M – PPh<sub>3</sub> – alkenyl – CO]<sup>+</sup>, 1258 (2) [M – 2PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 66.3; H, 4.8; N, 1.5. Calcd for C<sub>98</sub>H<sub>86</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 66.2; H, 4.9; N, 1.6.

[{**Ru**(CH=CHCPh<sub>2</sub>OH)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (5). This compound was prepared as for the synthesis of **3** using KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (15 mg, 0.048 mmol) and [Ru(CH=CHCPh<sub>2</sub>OH)(BTD)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (100 mg, 0.097 mmol) to provide a colorless powder. Yield: 43 mg (45%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1901 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 1914 ( $\nu_{CO}$ ), 1279, 1213, 1000 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.26–2.91 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 6.66 (m, 2 H, H<sub>β</sub>), 7.30 – 7.50 (m, 80 H + 2 H, C<sub>6</sub>H<sub>5</sub> + H<sub>α</sub>), (OH not observed) pm. <sup>31</sup>P NMR:  $\delta$  41.5 (s, PPh<sub>3</sub>) ppm. MS (FAB, MALDI): not diagnostic. Anal. Found: C, 66.8; H, 5.6; N, 1.5. Calcd for C<sub>110</sub>H<sub>112</sub>N<sub>2</sub>O<sub>4</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 66.7; H, 5.7; N, 1.4.

 $[{Ru(CH=CHCO_2Me)(CO)(PPh_3)_2}_2(S_2CNC_4H_8NCS_2)]$  (6). KS<sub>2</sub>-CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (16 mg, 0.051 mmol) was dissolved in MeOH (10  $cm^3$ ) and [Ru(CH=CHCO<sub>2</sub>Me)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (80 mg, 0.103) mmol) was added in dichloromethane (20 cm<sup>3</sup>). After the mixture was stirred at room temperature for 20 min, the solvent volume was reduced by rotary evaporation, and the resulting white powder was filtered off, washed with ethanol  $(10 \text{ cm}^3)$  and hexane  $(10 \text{ cm}^3)$ , and dried under vacuum. Yield: 60 mg (68%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1917  $(\nu_{\rm CO})$ , 1659  $(\nu_{\rm C=0})$  cm<sup>-1</sup>. IR (Nujol): 1927  $(\nu_{\rm CO})$ , 1698, 1678  $(\nu_{\rm C=0})$ , 1534, 1278, 1250, 1214, 1147, 999 ( $\nu_{C-S}$ ), 911, 832 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 2.54-2.76 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 3.37 (s, 6 H, CH<sub>3</sub>), 5.50 (d, 2 H,  $H_{\beta}$ ,  ${}^{3}J_{HH} = 15.0 \text{ Hz}$ ), 7.26–7.47 (m, 60 H, C<sub>6</sub>H<sub>5</sub>), 9.47 (d, 2 H, H<sub>\alpha</sub>),  ${}^{3}J_{\rm HH} = 15.0$  Hz) ppm.  ${}^{31}$ P NMR:  $\delta$  39.4 (s(br), PPh<sub>3</sub>) ppm. MS (MALDI): m/z (%) 1574 (2) [M - alkenyl - 2CO]<sup>+</sup>, 1399 (6) [M  $-PPh_3 - 2CO]^+$ , 1313 (20)  $[M - alkenyl - PPh_3 - 2CO]^+$ . Anal. Found: C, 61.8; H, 4.5; N, 1.6. Calcd for C<sub>88</sub>H<sub>78</sub>N<sub>2</sub>O<sub>6</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 61.7; H, 4.6; N, 1.6.

[Ru(CH=CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (7). The complex [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (1000 mg, 1.050 mmol) was dissolved in dichloromethane (70 cm<sup>3</sup>), and HC≡CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup> (360 mg, 2.101 mmol) was added. After the mixture was stirred at room temperature for 1 h, ethanol (40 cm<sup>3</sup>) was added. On slow concentration under reduced pressure a pale yellow powder formed, which was filtered off, washed with ethanol (20 cm<sup>3</sup>) and hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 660 mg (73%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1933 ( $\nu_{CO}$ ), 1586 cm<sup>-1</sup>. IR (Nujol): 1933 ( $\nu_{CO}$ ), 1732, 1583, 1287, 1271, 1122, 1039, 836 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 0.15 (s, 6 H, SiCH<sub>3</sub>), 0.78 (s, 9 H, Bu<sup>t</sup>), 3.85 (d, 2 H, CH<sub>2</sub>,  ${}^{3}J_{H_{e}H}$ = 6.9 Hz), 4.82 (dtt, 1 H,  $H_{\beta}$ ,  ${}^{3}J_{H_{\alpha}H_{\beta}}$  = 12.2 Hz,  ${}^{3}J_{HH_{\beta}}$  = 6.9 Hz,  ${}^{4}J_{\rm PH_{\beta}} = 2.0$  Hz), 7.31–7.68 (m, 30 H, C<sub>6</sub>H<sub>5</sub>), 7.74 (dt, 1 H, H<sub>{\alpha}</sub>,  ${}^{3}J_{H_{\alpha}H_{\beta}} = 12.2 \text{ Hz}, {}^{3}J_{PH_{\alpha}} \text{ unresolved} \text{ ppm. } {}^{31}\text{P NMR: } \delta 30.2 \text{ (s, PPh}_{3})$ ppm. MS (ES): *m*/*z* (%) 825 (5) [M - Cl]<sup>+</sup>, 563 (95) [M - Cl -PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 64.3; H, 5.6. Calcd for C<sub>46</sub>H<sub>49</sub>ClO<sub>2</sub>P<sub>2</sub>RuSi: C, 64.2; H, 5.7.

[{Ru(CH=CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (8). This compound was prepared as for the synthesis of **6** using KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (18 mg, 0.057 mmol) and [Ru(CH= CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (7; 100 mg, 0.116 mmol) to yield an off-white powder. Yield: 60 mg (55%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1914 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 1915 ( $\nu_{CO}$ ), 1572, 1252, 1213, 1029, 999  $(\nu_{C-8}) \text{ cm}^{-1} \cdot {}^{1}\text{H NMR: } \delta -0.22 \text{ (s, 12 H, SiCH_3), 0.77 (s, 18 H, Bu'), 2.52-2.84 (m, 8 H, NC_4H_8N), 3.44 (d, 2 H, CH_2, {}^{3}J_{HH} = 5.8 \text{ Hz}), 4.91 (m, 2 H, H_{\beta}), 6.77 (m, 2H, H_{\alpha}), 7.26-7.54 (m, 60 H, C_6H_5) \text{ ppm. } {}^{31}\text{P NMR: } \delta 40.0 \text{ (s, PPh_3) ppm. MS (FAB): } m/z (\%) 1453 (3) [M - PPh_3 - alkenyl]^+. Anal. Found: C, 61.5; H, 5.6; N, 1.5. Calcd for C_{98}H_{106}N_2O_4P_4Ru_2S_4Si_2 \cdot 0.5CH_2Cl_2: C, 61.3; H, 5.6; N, 1.5.$ 

**[Ru(CH=CHFc)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (9).** The complex [RuHCl(CO)(P-Ph<sub>3</sub>)<sub>3</sub>] (500 mg, 0.525 mmol) was dissolved in dichloromethane (40 cm<sup>3</sup>) and ethanol (20 cm<sup>3</sup>). HC≡CFc (120 mg, 0.571 mmol) was added and the reaction mixture stirred for 2 h, and then more ethanol (15 cm<sup>3</sup>) was added. On slow concentration under reduced pressure a brown powder precipitated, which was filtered off, washed with hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 340 mg (68%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2036, 1933 ( $\nu_{CO}$ ), 1574 cm<sup>-1</sup>. IR (Nujol): 2026, 1925 ( $\nu_{CO}$ ), 1568, 1163, 1029, 969, 932, 820 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 3.78 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3.88 (s(br), 2 H, C<sub>5</sub>H<sub>4</sub>), 3.96 (s, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.39 (d, 1 H, H<sub>β</sub>, <sup>3</sup>J<sub>HH</sub> = 13.3 Hz), 7.37−7.54 (m, 30 H, C<sub>6</sub>H<sub>5</sub>), 7.74 (d, 1 H, H<sub>α</sub>, <sup>3</sup>J<sub>HH</sub> = 13.3 Hz) ppm. <sup>31</sup>P NMR: δ 29.6 (s, PPh<sub>3</sub>) ppm. MS (ES): *m*/*z* (%) 865 (100) [M − Cl]<sup>+</sup>. Anal. Found: C, 65.3; H, 4.3. Calcd for C<sub>49</sub>H<sub>41</sub>CIFeOP<sub>2</sub>Ru: C, 65.4; H, 4.6.

**[Os(CH=CHFc)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (10).** This compound was prepared as for the synthesis of **9** using [OsHCl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (500 mg, 0.546 mmol) and HC≡CFc (126 mg, 0.600 mmol) to provide a dark purple product. Yield: 510 mg (83%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2022, 1906 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2022, 1910 ( $\nu_{CO}$ ), 1574, 1537, 1096, 954, 827, 746, 701 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 3.95 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.08 (s(br), 2 H, C<sub>5</sub>H<sub>4</sub>), 4.30 (s(br), 2 H, C<sub>5</sub>H<sub>4</sub>), 6.28 (d, 1 H, H<sub>β</sub>, <sup>3</sup>J<sub>HH</sub> = 15.5 Hz), 6.80−7.69 (m, 30 H + 4 H, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>4</sub>), 9.05 (d, 1 H, H<sub>α</sub>, <sup>3</sup>J<sub>HH</sub> = 15.5 Hz) ppm. <sup>31</sup>P NMR: δ −3.0 (s, PPh<sub>3</sub>) ppm. MS (ES): not diagnostic. Anal. Found: C, 58.6; H, 4.1; N, 2.2. Calcd for C<sub>55</sub>H<sub>45</sub>CIFeN<sub>2</sub>OOsP<sub>2</sub>S: C, 58.7; H, 4.0; N, 2.5.

[{**Ru**(CH=CHFc)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (11). This compound was prepared as for the synthesis of **6** using KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (9 mg, 0.029 mmol) and [Ru(CH=CHFc)-Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**9**; 50 mg, 0.056 mmol) to yield a light brown powder. Yield: 42 mg (76%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2029, 1913 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2025, 1916 ( $\nu_{CO}$ ), 1213, 1027, 999 ( $\nu_{C-S}$ ), 812 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.56–2.82 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 3.89 (s(br), 4 H, C<sub>5</sub>H<sub>4</sub>), 3.95 (s(br), 4 H, C<sub>5</sub>H<sub>4</sub>), 3.97 (s, 10 H, Cp), 5.84 (d, 2 H, H<sub>β</sub>, <sup>3</sup>J<sub>HH</sub> = 15.6 Hz), 6.97–7.87 (m, 60 H, C<sub>6</sub>H<sub>5</sub>), 7.70 (dt, 2 H, H<sub>α</sub>, <sup>3</sup>J<sub>HH</sub> = 15.6 Hz, J<sub>HP</sub> unresolved) ppm. <sup>31</sup>P NMR:  $\delta$  39.8 (s, PPh<sub>3</sub>) ppm. MS (FAB): m/z (%) 1967 (2) [M]<sup>+</sup>, 1705 (2) [M – PPh<sub>3</sub>]<sup>+</sup>, 1443 (1) [M – 2PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 61.1; H, 4.4; N, 1.6. Calcd for C<sub>104</sub>H<sub>90</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub> • CH<sub>2</sub>Cl<sub>2</sub>: C, 61.5; H, 4.5; N, 1.4.

[{Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (12). This compound was prepared as for the synthesis of **3** using KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (15 mg, 0.048 mmol) and [Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(BTD)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (100 mg, 0.097 mmol) to yield a yellow powder. Yield: 83 mg (88%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1898 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 1901 ( $\nu_{CO}$ ), 1279, 1216, 1027, 999 ( $\nu_{C-S}$ ), 950, 840 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.20 (s, 6 H, CH<sub>3</sub>), 2.62–2.97 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 5.58 (d, 2 H, H<sub>β</sub>, <sup>3</sup>J<sub>HH</sub> = 15.0 Hz), 6.38, 6.80 ((AB)<sub>2</sub>, 8 H, C<sub>6</sub>H<sub>4</sub>, J<sub>AB</sub> = 6.0 Hz), 7.33–7.80 (m, 60 H, C<sub>6</sub>H<sub>5</sub>), 8.31 (d, 2 H, H<sub>α</sub>, <sup>3</sup>J<sub>HH</sub> = 15.0 Hz) ppm. <sup>31</sup>P NMR:  $\delta$  8.3 (s, PPh<sub>3</sub>) ppm. MS (FAB): *m/z* (%) 1957 (1) [M]<sup>+</sup>, 1697 (1) [M – PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 60.3; H, 4.3; N, 1.5. Calcd for C<sub>98</sub>H<sub>86</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 60.2; H, 4.4; N, 1.4.

[{Os(C(C=CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (13). KS<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>K (14 mg, 0.045 mmol) was dissolved in MeOH (15 cm<sup>3</sup>), and the complex [Os(C(C=CPh)=CHPh)Cl-(BTD)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (100 mg, 0.089 mmol) was added in dichloromethane (20 cm<sup>3</sup>). After the mixture was stirred at room temperature for 20 min, the solvent was removed by rotary evaporation. The crude product was not sufficiently soluble, and so after trituration in ethanol the yellow product was filtered off, washed with ethanol (10 cm<sup>3</sup>) and hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 90 mg (95%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2152 ( $\nu_{C=C}$ ), 1902 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2154 ( $\nu_{C=C}$ ), 1905 ( $\nu_{CO}$ ), 1592, 1215, 999 ( $\nu_{C-S}$ ), 948 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.02–2.78 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 6.32 (s(br), 2 H, H<sub>β</sub>), 6.88–7.54 (m, 70 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR:  $\delta$  6.6 (s, PPh<sub>3</sub>) ppm. MS (FAB) not diagnostic. Anal. Found: C, 63.0; H, 4.6; N, 1.2. Calcd for C<sub>112</sub>H<sub>90</sub>N<sub>2</sub>O<sub>2</sub>O<sub>2</sub>O<sub>8</sub>P<sub>4</sub>S<sub>4</sub>: C, 63.2; H, 4.3; N, 1.3.

 $\{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2\}(S_2CNC_4H_8NCS_2)\{Ru (CH=CHBu^{t})(CO)(PPh_{3})_{2}$  (14). A dichloromethane (20 cm<sup>3</sup>) solution of [Ru(C(C=CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 150 mg, 0.142 mmol) was treated with triethylamine (4 drops, excess) and  $CS_2$  (4 drops, excess). After the mixture was stirred for 5 min, [Ru(CH=CHBu<sup>t</sup>)Cl(BTD)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (129 mg, 0.142 mmol) in dichloromethane (15 cm<sup>3</sup>) was added and this mixture was stirred for 15 min and then filtered through diatomaceous earth. Ethanol (15 cm<sup>3</sup>) was added, and a yellow-brown powder was obtained by concentration under reduced pressure. It was filtered off, washed with hexane (15 cm<sup>3</sup>), and dried under vacuum. Yield: 170 mg (65%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2152 ( $\nu_{C=C}$ ), 1912 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2152 ( $\nu_{C=C}$ ), 1916 ( $\nu_{CO}$ ), 1596, 1279, 1213, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.34 (s, 9 H, Bu<sup>t</sup>), 2.42–2.92 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 4.54 (d, 1 H, =CHBu<sup>t</sup>,  ${}^{3}J_{HH} = 16.4$  Hz), 6.21 (s(br), 1 H, =CHPh), 6.28 (d, 1 H, RuCH,  ${}^{3}J_{HH} = 16.5$  Hz), 6.93–7.70 (m, 70 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ 38.0 (s, PPh<sub>3</sub>, Ru-enynyl), 40.6 (s, PPh<sub>3</sub>, Ru-alkenylBu<sup>t</sup>) ppm. MS (FAB): *m/z* (%) 1693 (1)  $[M - alkenyl - 2CO]^+$ , 1568 (1)  $[M - PPh_3]^+$ , 1483 (2)  $[M - PPh_3]^+$ alkenyl – PPh<sub>3</sub>]<sup>+</sup>, 1365 (3) [M – PPh<sub>3</sub> – enynyl]<sup>+</sup>, 1303 (4) [M - 2 PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 66.9; H, 4.9; N, 1.4. Calcd for C<sub>102</sub>H<sub>90</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 66.9; H, 5.0; N, 1.5.

 $[{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2}(S_2CNC_4H_8NCS_2){Ru-$ (CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub>]] (15). This compound was prepared as for the synthesis of 14 using [Ru(C(C=CPh)=CHPh) (S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 100 mg, 0.095 mmol), triethylamine (4 drops, excess), CS<sub>2</sub>(2 drops, excess), and [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(BTD)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (89 mg, 0.094 mmol) to yield an orange powder. Yield: 110 mg (62%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2154 ( $\nu_{C=C}$ ), 1925  $(\nu_{\rm CO})$  cm<sup>-1</sup>. IR (Nujol): 2148 ( $\nu_{\rm C=C}$ ), 1920 ( $\nu_{\rm CO}$ ), 1591, 1231, 1001  $(\nu_{C-S})$ , 917, 847 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.26 (s, 3 H, CH<sub>3</sub>), 2.44-3.12 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 5.67 (d, 1 H, =CHC<sub>6</sub>H<sub>4</sub>Me-4,  ${}^{3}J_{HH}$ = 15.3 Hz), 6.27 (s(br), 1 H, =CHPh), 6.76, 6.92 ((AB)<sub>2</sub>, 4 H,  $C_6H_4$ ,  $J_{AB} = 7.7$  Hz), 7.02–7.97 (m, 70 H,  $C_6H_5$ ), 8.45 (d, 1 H, RuCH,  ${}^{3}J_{HH} = 15.2$  Hz) ppm.  ${}^{31}P$  NMR:  $\delta$  27.8 ppm (s, PPh<sub>3</sub>, Ru-tolyl), 37.6 (s, PPh<sub>3</sub>, Ru-enynyl). MS (MALDI): *m/z* (%) 1749 (1)  $[M - alkenyl]^+$ , 1487 (1)  $[M - alkenyl - PPh_3]^+$ , 1200 (2)  $[M - alkenyl - 2PPh_3 - CO]^+$ , 1022 (3) [M - alkenyl - enynyl]- 2PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 67.3; H, 4.6; N, 1.4. Calcd for C<sub>105</sub>H<sub>88</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 67.7; H, 4.8; N, 1.5.

 $[\{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2\}(S_2CNC_4H_8NCS_2)\{Ru-$ (CH=CHCPh<sub>2</sub>OH)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (16). This compound was prepared as for the synthesis of 14 using [Ru(C(C=CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 80 mg, 0.076 mmol), triethylamine (4 drops, excess), CS<sub>2</sub> (2 drops, excess), and [Ru(CH=CHCPh<sub>2</sub>OH)Cl(BTD)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (78 mg, 0.075 mmol) to provide an orange-brown powder. Yield: 100 mg (67%). IR  $(CH_2Cl_2)$ : 2152 ( $\nu_{C=C}$ ), 1924 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2147, 1922  $(\nu_{\rm CO})$ , 1593, 1279, 1231, 1187, 999  $(\nu_{\rm C-S})$ , 911 cm<sup>-1</sup>. <sup>1</sup>H NMR ( $d_6$ -acetone):  $\delta$  2.40–3.09 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 5.12 (d, 1 H, =CHCPh<sub>2</sub>OH,  ${}^{3}J_{HH}$  = 15.5 Hz), 6.35 (s, 1 H, =CHPh), 7.02-7.69 (m, 80 H, C<sub>6</sub>H<sub>5</sub>), 8.03 (m, 1 H, RuCH) ppm.  $^{31}\mathrm{P}$  NMR:  $\delta$  34.0 (s, PPh<sub>3</sub>, Ru-hydroxyalkenyl), 37.5 (s, PPh<sub>3</sub>, Ru-enynyl) ppm. MS (FAB): m/z (%) 1951 (1) [M]<sup>+</sup>, 1521 (2) [M – alkenyl – enynyl - CO]<sup>+</sup>. Anal. Found: C, 68.1; H, 4.8; N, 1.5. Calcd for C<sub>111</sub>H<sub>92</sub>N<sub>2</sub>O<sub>3</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 68.2; H, 4.7; N, 1.4.

[{Ru(C(C=CPh)=CHPh)(CO)(PPh\_3)\_2}(S\_2CNC\_4H\_8NCS\_2){Ru-(CH=CHCO\_2Me)(CO)(PPh\_3)\_2}] (17). This compound was prepared as for the synthesis of 14 using [Ru(C(C=CPh)=CHPh)(S\_2CNC\_4H\_8NH\_2)(CO)(PPh\_3)\_2]Cl (1; 100 mg, 0.095)

mmol), triethylamine (4 drops, excess), CS<sub>2</sub> (2 drops, excess), and [Ru(CH=CHCO<sub>2</sub>Me)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (73 mg, 0.094 mmol) to give an olive green product. Yield: 102 mg (59%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2152 ( $\nu_{C=C}$ ), 1926 ( $\nu_{CO}$ ) 1692, 1670 ( $\nu_{C=O}$ ) cm<sup>-1</sup>. IR (Nujol): 2152 ( $\nu_{C=C}$ ), 1922 ( $\nu_{CO}$ ), 1694, 1678 ( $\nu_{C=O}$ ), 1278, 1214, 999 ( $\nu_{C-S}$ ), 911, 831 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.20–2.97 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 3.21 (s, 3 H, CH<sub>3</sub>), 5.41 (d, 1 H, =CHCO<sub>2</sub>Me,  $J_{HH}$  = 16.1 Hz), 6.21 (s(br), 1 H, =CHPh), 6.92–7.63 (m, 70 H, C<sub>6</sub>H<sub>5</sub>), 9.35 (d, 1 H, RuCH,  $J_{HH}$  = 16.1 Hz) ppm. <sup>31</sup>P NMR:  $\delta$  37.8 (s, PPh<sub>3</sub>, Ru–enynyl), 39.4 (s, PPh<sub>3</sub>, Ru–CH=CHCO<sub>2</sub>Me) ppm. MS (FAB): m/z (%) 1834 (1) [M]<sup>+</sup>, 1570 (1) [M – PPh<sub>3</sub>], 1484 (2) [M – PPh<sub>3</sub> – alkenyl]. Anal. Found: C, 65.5; H, 4.7; N, 1.7. Calcd for C<sub>100</sub>H<sub>84</sub>N<sub>2</sub>O<sub>4</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 65.6; H, 4.6; N, 1.5.

 $[{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2}(S_2CNC_4H_8NCS_2){Ru-$ (CH=CHCH<sub>2</sub>OSiMe<sub>2</sub>Bu<sup>t</sup>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]] (18). This compound was prepared as for the synthesis of 14 using [Ru(C(C=CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 100 mg, 0.095 mmol), triethylamine (4 drops, excess), CS<sub>2</sub> (2 drops, excess), and  $[Ru(CH=CHCH_2OSiMe_2Bu^{t})Cl(CO)(PPh_3)_2]$ (7; 82 mg, 0.095 mmol) to yield a yellow-green product. Yield: 110 mg (60%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2153 ( $\nu_{C=C}$ ), 1920 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2147 ( $\nu_{C=C}$ ), 1917 ( $\nu_{CO}$ ), 1591, 1213, 999 ( $\nu_{C-S}$ ), 891 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  -0.18,  $(s, 6 H, CH_3), 0.74 (s, 9 H, Bu<sup>t</sup>), 2.16 - 3.14 (m, 8 H, NC_4H_8N),$ 3.46 (s(br), 2 H, CH<sub>2</sub>), 4.92 (m, 1 H, =CHCO), 6.25 (s(br), 1 H, =CHPh), 6.76 (m, 1 H, RuCH), 6.92-7.55 (m, 70 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR:  $\delta$  37.7 (s, PPh<sub>3</sub>, Ru–enynyl), 40.1 (s, PPh<sub>3</sub>, Ru–alkenylSi) ppm. MS (FAB): m/z (%) 1890 (1) [M - CO]<sup>+</sup>, 1390 (2) [M -2PPh3]<sup>+</sup>. Anal. Found: C, 65.5; H, 5.1; N, 1.4. Calcd for C<sub>105</sub>H<sub>98</sub>N<sub>2</sub>O<sub>3</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>Si: C, 65.7; H, 5.2; N, 1.5.

[{Ru(C(C=CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>}(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>){Ru-(CH=CHFc)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (19). This compound was prepared as of 14 using  $[Ru(C(C \equiv CPh) =$ for the synthesis CHPh)(S2CNC4H8NH2)(CO)(PPh3)2]Cl (1; 59 mg, 0.056 mmol), triethylamine (3 drops, excess), CS<sub>2</sub> (2 drops, excess), and  $[Ru(CH=CHFc)Cl(CO)(PPh_3)_2]$  (9; 50 mg, 0.056 mmol) to yield a yellow-green product. Yield: 80 mg (73%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2151  $(\nu_{C=C})$ , 1922  $(\nu_{CO})$  cm<sup>-1</sup>. IR (Nujol): 2154  $(\nu_{C=C})$ , 1917  $(\nu_{CO})$ , 1589, 1213, 1186, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.65–3.18 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 3.63, 3.83 (s(br)  $\times$  2, 4 H, C<sub>5</sub>H<sub>4</sub>), 3.73 (s, 5 H, Cp), 6.30 (s(br), 1 H, =CHPh), 6.32 (d, 1 H, =CHFc,  $J_{\rm HH} = 17.0$ Hz), 6.93–7.68 (m, 70 H + 1 H,  $C_6H_5$  + RuCH) ppm. <sup>31</sup>P NMR  $(CD_2Cl_2)$ :  $\delta$  37.8 (s, PPh<sub>3</sub>, Ru–enynyl), 39.3 (s, PPh<sub>3</sub>, Ru–alkenylFc) ppm. MS (FAB): m/z (%) 1540 (1) [M - alkenyl - enynyl]<sup>+</sup>, 1380 (2)  $[M - 2PPh_3 - 2CO]^+$ . Anal. Found: C, 66.2; H, 4.5; N, 1.6. Calcd for C<sub>108</sub>H<sub>90</sub>FeN<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 66.3; H, 4.6; N, 1.4.

 $[\{Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2\}(S_2CNC_4H_8NCS_2)\{Os (CH=CHC_6H_4Me-4)(CO)(PPh_3)_2$ ] (20). This compound was prepared as for the synthesis of 14 using [Ru(C(C=-CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 100 mg, 0.095 mmol), triethylamine (5 drops, excess), CS<sub>2</sub> (3 drops, excess), and [Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(BTD)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (98 mg, 0.095 mmol) to provide an orange product. Yield: 106 mg (57%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2150 ( $\nu_{C=C}$ ), 1927 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2149 ( $\nu_{C=C}$ ), 1925 ( $\nu_{CO}$ ), 1592, 1278, 1215, 999 ( $\nu_{C-S}$ ), 910 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.22 (s, 3 H, CH<sub>3</sub>), 2.55–2.89 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 5.55 (d, 1 H, =CHC<sub>6</sub>H<sub>4</sub>Me-4,  ${}^{3}J_{\rm HH} = 15.6$  Hz), 6.24 (s(br), 1 H, =CHPh), 6.32, 6.81 ((AB)<sub>2</sub>, 4 H, C<sub>6</sub>H<sub>4</sub>,  $J_{AB} = 7.4$  Hz), 6.93–7.56 (m, 70 H, C<sub>6</sub>H<sub>5</sub>), 8.26 (d, 1 H, RuCH,  ${}^{3}J_{\text{HH}} = 15.6$  Hz) ppm.  ${}^{31}\text{P}$  NMR:  $\delta$  8.1 (s, OsPPh<sub>3</sub>), 38.0 (s, RuPPh<sub>3</sub>) ppm. MS (FAB): *m/z* (%) 1953 (2) [M]<sup>+</sup>, 1692 (6)  $[M - PPh_3]^+$ , 1574 (7)  $[M - PPh_3 - alkenyl]^+$  1429 (5)  $[M - PPh_3 - alkenyl]^+$ 2PPh3]<sup>+</sup>. Anal. Found: C, 64.3; H, 4.4; N, 1.5. Calcd for C<sub>105</sub>H<sub>88</sub>N<sub>2</sub>O<sub>2</sub>OsP<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 64.6; H, 4.5; N, 1.4.

 $[Ru(C(C \equiv CPh) = CHPh)(CO)(PPh_3)_2(S_2CNC_4H_8NCS_2)Os-(CH=CHFc)(CO)(PPh_3)_2]$  (21). This compound was prepared as for the synthesis of 14 using  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]Cl (1) (190 mg, 0.180 mmol), triethylamine (4 drops, excess), CS<sub>2</sub> (3 drops, excess) and$ 

[Os(CH=CHFc)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (**10**) (200 mg, 0.178 mmol), stirred for 2 h, to give a black product. Yield: 310 mg (84%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2152 ( $\nu_{C=C}$ ), 2022, 1927 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2149 ( $\nu_{C=C}$ ), 1924 ( $\nu_{CO}$ ), 1591, 1216, 1188, 1279, 1000 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta$  3.43–4.00 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 4.21 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.57, 4.73 (s(br) × 2, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.35 (s, 1 H, =CHPh), 6.46 (d, 1 H, =CHFc, <sup>3</sup>J<sub>HH</sub> = 15.0 Hz), 6.90–7.70 (m, 70 H, C<sub>6</sub>H<sub>5</sub>), 8.04 (dt, 1 H, OsCH, <sup>3</sup>J<sub>HH</sub> = 15.0 Hz, J<sub>HP</sub> unresolved) ppm. <sup>31</sup>P NMR:  $\delta$  7.9 (s, OsPPh<sub>3</sub>), 37.9 (s, RuPPh<sub>3</sub>) ppm. MS (LSIMS): *m/z* (%) 1784 (1) [M – PPh<sub>3</sub>]<sup>+</sup>, 1524 (4) [M – 2PPh<sub>3</sub>]<sup>+</sup>. Anal. Found: C, 63.3; H, 4.4; N, 1.4. Calcd for C<sub>108</sub>H<sub>90</sub>FeN<sub>2</sub>O<sub>2</sub>OsP<sub>4</sub>RuS<sub>4</sub>: C, 63.4; H, 4.4; N, 1.4.

 $[Ru(C(C \equiv CPh) = CHPh)(CS)(PPh_3)_2(S_2CNC_4H_8NH_2)]Cl (22).$ The reagent S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub> (13 mg, 0.080 mmol) was dissolved in methanol (8 cm<sup>3</sup>), and the complex [Ru(C(C=CPh)=CHPh)Cl(CS)(PPh<sub>3</sub>)<sub>2</sub>] (50 mg, 0.055 mmol) in dichloromethane (20 cm<sup>3</sup>) was added. After the mixture was stirred at room temperature for 1 h, during which a change from orange to yellow was observed, the volatiles were removed. The crude product was dissolved in a small amount of dichloromethane, and ethanol (10 cm<sup>3</sup>) was added. Slow concentration under reduced pressure gave a yellow product, which was filtered off, washed with hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 40 mg (68%). IR  $(CH_2Cl_2)$ : 2145 ( $\nu_{C=C}$ ) cm<sup>-1</sup>. IR (Nujol): 2150 ( $\nu_{C=C}$ ), 1246 ( $\nu_{CS}$ ), 999 ( $\nu_{C-S}$ ), 893, 846 cm<sup>-1</sup>. NMR ( $d_6$ -acetone) <sup>1</sup>H:  $\delta$  3.10, 3.31 (s  $\times$  2, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 6.42 (s, 1 H, H<sub>β</sub>), 6.69–7.45 (m, 40 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR: 37.0 (s, PPh<sub>3</sub>) ppm. MS (FAB): *m/z* (%) 1035 (1) [M]<sup>+</sup>. Anal. Found: C, 64.9; H, 4.8; N, 2.7. Calcd for C<sub>58</sub>H<sub>51</sub>N<sub>2</sub>P<sub>2</sub>RuS<sub>3</sub>: C, 65.1; H, 4.8; N, 2.6.

[{**Ru**(**C**(**C≡CPh**)**=CHPh**)(**CO**)(**PPh**<sub>3</sub>)<sub>2</sub>)(**S**<sub>2</sub>**CNC**<sub>4</sub>**H**<sub>8</sub>**NCS**<sub>2</sub>){**Ru**-(**C**(**C≡CPh**)**=CHPh**)(**CS**)(**PPh**<sub>3</sub>)<sub>2</sub>]] (23). This compound was prepared as for the synthesis of **14** using [Ru(C(**C≡** CPh)**=**CHPh)(**S**<sub>2</sub>CNC<sub>4</sub>**H**<sub>8</sub>**NH**<sub>2</sub>)(CS)(PPh<sub>3</sub>)<sub>2</sub>]Cl (**22**; 50 mg, 0.047 mmol), triethylamine (1 drop, excess), CS<sub>2</sub> (1 drop, excess), and [Ru(C(**C≡**CPh)**=**CHPh)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (42 mg, 0.047 mmol) to give a yellow-brown product. Yield: 67 mg (73%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2153 ( $\nu_{C=C}$ ), 1923 ( $\nu_{C0}$ ), 1606 cm<sup>-1</sup>. IR (Nujol): 2150 ( $\nu_{C=C}$ ), 1921 ( $\nu_{C0}$ ), 1592, 1259 ( $\nu_{CS}$ ), 1260, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.08−3.25 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 6.35 (s(br), 2 H, H<sub>β</sub>), 6.92−7.99 (m, 80 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR: δ 34.1 (s(br), PPh<sub>3</sub>) ppm. MS (MALDI): m/z (%) 1702 (2) [M − PPh<sub>3</sub>]<sup>+</sup>, 1557 (2) [M − 2(enynyl)]<sup>+</sup>. Anal. Found: C, 68.3; H, 4.4; N, 1.2. Calcd for C<sub>112</sub>H<sub>90</sub>N<sub>2</sub>OP<sub>4</sub>Ru<sub>2</sub>S<sub>5</sub>: C, 68.4; H, 4.6; N, 1.4.

[{Ru(C=CBu<sup>t</sup>)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)] (24). [{Ru(CH=  $CHC_6H_4Me-4)(CO)(PPh_3)_2\}_2(S_2CNC_4H_8NCS_2)]$  (4; 80 mg, 0.045 mmol) and HC=CBut (28 mg, 0.341 mmol) were heated under reflux in toluene for 3 h. All solvent was removed under reduced pressure, the product was taken up in a small amount of dichloromethane, and this mixture was filtered through diatomaceous earth. Ethanol (15 cm<sup>3</sup>) was added, and a tan powder was obtained by reducing the solvent volume. This was filtered off, washed with hexane (10 cm<sup>3</sup>), and dried under vacuum. Yield: 54 mg (70%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2103 ( $\nu_{C=C}$ ), 1941 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2102  $(ν_{C=C})$ , 1947  $(ν_{CO})$ , 1279, 1215 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.94 (s, 18 H, Bu<sup>t</sup>), 1.95–2.24 (m, 8 H, NC<sub>4</sub>H<sub>8</sub>N), 6.73–7.89 (m, 60 H,  $C_6H_5)$  ppm.  $^{31}\text{P}$  NMR:  $\delta$  38.9, 39.3 (s  $\times$  2, PPh\_3) ppm. MS (MALDI): m/z (%) 1706 (2) [M]<sup>+</sup>, 1444 (2) [M – PPh<sub>3</sub>]<sup>+</sup>, 1418 (4)  $[M - CO - PPh_3]^+$ , 1307 (4)  $[M - alkynyl - 2CO - PPh_3]^+$ . Anal. Found: C, 61.8; H, 4.7; N, 1.9. Calcd for  $C_{92}H_{86}N_2O_2P_4Ru_2S_4 \cdot 1.5CH_2Cl_2$ : C, 61.3; H, 4.9; N, 1.5.

[{Ru(C(C=CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)}<sub>2</sub>Ni] (25). [Ru(C(C=CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 80 mg, 0.076 mmol) was dissolved in dichloromethane (15 cm<sup>3</sup>) and methanol (8 cm<sup>3</sup>). Triethylamine (4 drops, excess) and CS<sub>2</sub> (3 drops, excess) were added. After the mixture was stirred for 5 min, [Ni(O<sub>2</sub>CMe)<sub>2</sub>] (6.7 mg, 0.038 mmol) in dichloromethane (5 cm<sup>3</sup>) was added, the mixture was stirred for 2 h, and all solvent was

 Table 1. Crystal Data and Structure Refinement Parameters for

 1 • 1.25EtOH

1 1120	lion
chem formula	C <sub>60.5</sub> H <sub>58.5</sub> ClN <sub>2</sub> O <sub>2.25</sub> P <sub>2</sub> RuS <sub>2</sub>
Iw	1112.17
cryst syst	monoclinic
cryst color	yellow
cryst size (mm)	$0.22 \times 0.17 \times 0.02$
space group	$P2_1/c$
a (Å)	21.2542(6)
b (Å)	16.2199(5)
<i>c</i> (Å)	18.9949(6)
α (deg)	90
$\beta$ (deg)	105.006(2)
$\gamma$ (deg)	90
$V(Å^3)$	6325.0(3)
Ζ	4
$D_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.168
<i>T</i> (K)	150(2)
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.446
F(000)	2306
no. of rflns collected	40 498
no. of unique rflns/data ( $R_{int}$ )	13 562/698 (0.0817)
R1 $(I > 2\sigma(I))$	0.0698
wR2 $(I > 2\sigma(I))$	0.1697
R1 (all data)	0.1196
wR2 (all data)	0.1974

then removed under reduced pressure. The yellow product was taken up in a small amount of dichloromethane and filtered through diatomaceous earth. Ethanol (10 cm<sup>3</sup>) was added,and the solvent volume was reduced by rotary evaporation. The product was filtered off, washed with hexane (15 cm<sup>3</sup>), and dried under vacuum. Yield: 47 mg (55%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2152 ( $\nu_{C=C}$ ), 1926 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2152 ( $\nu_{C=C}$ ), 1925 ( $\nu_{CO}$ ), 1592, 1278, 1216, 1157, 999 ( $\nu_{C-S}$ ), 908 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.08–3.29 (m, 16 H, NC<sub>4</sub>H<sub>8</sub>N), 6.30 (s, 2 H, H<sub>β</sub>), 6.93–7.55 (m, 80 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR:  $\delta$  38.0 (s, PPh<sub>3</sub>) ppm. MS (FAB): m/z (%) 1691 (2) [M – 2PPh<sub>3</sub> – CO]<sup>+</sup>. Anal. Found: C, 63.0; H, 4.3; N, 2.5. Calcd for C<sub>118</sub>H<sub>98</sub>N<sub>4</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>8</sub>Ni: C, 63.1; H, 4.4; N, 2.5.

[{**Ru**(C(C≡CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)}<sub>2</sub>Pd] (26). This compound was prepared as for the synthesis of 25 using [Ru(C(C≡CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 80 mg, 0.076 mmol), triethylamine (4 drops, excess), CS<sub>2</sub> (2 drops, excess), and [PdCl<sub>2</sub>(NCMe)<sub>2</sub>] (9.8 mg, 0.038 mmol) to provide a brown product. Yield: 49 mg (56%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2152 ( $\nu_{C=C}$ ), 1927 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2152 ( $\nu_{C=C}$ ), 1921 ( $\nu_{CO}$ ), 1592, 1277, 1217, 1158, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 2.82–3.40 (m, 16 H, NC<sub>4</sub>H<sub>8</sub>N), 6.28 (s, 2 H, H<sub>β</sub>), 6.92–7.67 (m, 80 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P NMR: δ 38.0 (s, PPh<sub>3</sub>) ppm. MS (FAB): *m/z* (%) 1859 (1) [M – 2 alkenyl – CO]<sup>+</sup>, 1199 (1) [M – Ru(C(C≡CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Found: C, 61.8; H, 4.3; N, 2.5. Calcd for C<sub>118</sub>H<sub>98</sub>N<sub>4</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>8</sub>Pd: C, 61.8; H, 4.3; N, 2.4.

[{**Ru**(C(C≡CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)}<sub>2</sub>Pt] (27). This compound was prepared as for the synthesis of **25** using [Ru(C(C≡CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 50 mg, 0.047 mmol), triethylamine (3 drops, excess), CS<sub>2</sub> (2 drops, excess), and [PtCl<sub>2</sub>(NCPh)<sub>2</sub>] (11.2 mg, 0.024 mmol) to yield a yellow product. Yield: 32 mg (56%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2153 ( $\nu_{C=C}$ ), 1931 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2152 ( $\nu_{C=C}$ ), 1928 ( $\nu_{CO}$ ), 1278, 1217, 1158, 1000 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 2.78−3.30 (m, 16 H, NC<sub>4</sub>H<sub>8</sub>N), 6.30 (s, 2 H, H<sub>β</sub>), 6.85−7.72 (m, 80 H, C<sub>6</sub>H<sub>3</sub>) ppm. <sup>31</sup>P NMR: δ 38.1 (s, PPh<sub>3</sub>) ppm. MS (FAB): *m/z* (%) 2177 (2) [M − enynyl]<sup>+</sup>, 1981 (1) [M − 2 enynyl]<sup>+</sup>, 1687 (1) [M − 2 enynyl − PPh<sub>3</sub> − CO]<sup>+</sup>, 1550 (2) [M − Ru(enynyl)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Found: C, 59.4; H, 4.3; N, 2.3. Calcd for C<sub>118</sub>H<sub>98</sub>N<sub>4</sub>O<sub>2</sub>P<sub>4</sub>PtRu<sub>2</sub>S<sub>8</sub>: C, 59.5; H, 4.2; N, 2.4.

[{Ru(C(C=CPh)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)}<sub>2</sub>Zn] (28). This compound was prepared as for the synthesis of 25 using [Ru(C(C=CPh)=CHPh)(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]Cl (1; 50 mg, 0.047 mmol), triethylamine (3 drops, excess), CS<sub>2</sub> (2 drops, excess), and [Zn(O<sub>2</sub>CMe)<sub>2</sub>] • 2H<sub>2</sub>O (5.2 mg, 0.024 mmol) to yield a yellow product. Yield: 55 mg (52%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2152 ( $\nu_{C=C}$ ), 1926 ( $\nu_{CO}$ ) cm<sup>-1</sup>. IR (Nujol): 2152 ( $\nu_{C=C}$ ), 1923 ( $\nu_{C0}$ ), 1573, 1277, 1214, 1155, 999 ( $\nu_{C-S}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.62–3.61 (m, 16 H, NC<sub>4</sub>H<sub>8</sub>N), 6.25 (s, 2 H, H<sub>β</sub>), 6.89–7.51 (m, 80 H, C<sub>6</sub>H<sub>3</sub>) ppm. <sup>31</sup>P NMR:  $\delta$  38.0 (s, PPh<sub>3</sub>) ppm. MS (FAB): *m/z* (%) 1397 (1) [M – Ru(enynyl)-(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Found: C, 59.5; H, 3.8; N, 2.4. Calcd for C<sub>118</sub>H<sub>98</sub>N<sub>4</sub>O<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>8</sub>Zn • 2CH<sub>2</sub>Cl<sub>2</sub>: C, 59.5; H, 4.2; N, 2.3.

**Crystallographic Studies.** Crystals of 1 were grown by slow diffusion of ethanol into a dichloromethane solution of the complex and subsequent slow evaporation. Single-crystal X-ray diffraction data were collected using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710$  73 Å) on an Enraf-Nonius KappaCCD diffractometer equipped with a Cryostream N<sub>2</sub> open-flow cooling device<sup>33</sup> at 150(2) K. Series of  $\omega$  scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.77 Å.

Cell parameters and intensity data for **1** were processed using the DENZO-SMN package,<sup>34</sup> and the structure was solved by direct methods and refined by full-matrix least squares on  $F^2$  using SHELXTL software.<sup>35</sup> Intensities were corrected for absorption effects by the multiscan method based on multiple scans of identical and Laue equivalent reflections (using the SORTAV software).<sup>36</sup>

Where possible, non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were

(34) Otwinowski, Z.; Minor, W. In *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1997; Methods in Enzymology 276.

(35) SHELXTL, version 5.1; Bruker Analytical X-ray Instruments Inc., Madison, WI, 1999.

positioned geometrically and refined using a riding model. In addition to the  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)-(PPh_3)_2]^+$  (1) cation, there are also disordered solvent molecules and chloride counteranions which were located in the difference map. The chloride ion was refined using a model where it was split over three sites with occupancies of 0.65, 0.18, and 0.17 for Cl1, Cl1A, and Cl1B, respectively. Five partially occupied ethanol molecules were clearly visible in the difference map and refined with 25% occupancy each, using the same distance restraint to maintain plausible geometries. Crystal data and structure refinement parameters are included in Table 1.

Crystallographic data (excluding structure factors) for the structure of **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 677008). Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Acknowledgment. J.D.E.T.W.-E. gratefully acknowledges Merton College for the provision of a Fellowship. We thank the OUP John Fell Fund for consumables and Johnson Matthey Ltd for a generous loan of ruthenium and osmium salts.

**Supporting Information Available:** A CIF file giving crystallographic data for the structure of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800686F

<sup>(33)</sup> Cosier, J.; Glazer, A. M. J. Appl. Crystallogr. 1986, 19, 105.

<sup>(36)</sup> Blessing, R. H. Acta Crystallogr. 1995, A51, 33-38.