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Reactions of the Trinuclear Cluster (μ_2-H)Ru$_3$(CO)$_9$(μ_3,η^2-SCNHPhNPh): Synthesis and Molecular Structure of Ru$_3$(CO)$_6$(PPh$_3$)(μ_2,η^2-C$_6$H$_5$)-(μ_2-PPh$_2$)(μ_3-S), a Complex Containing a Phenyl Ligand with a Rare σ,π-Coordination Mode†

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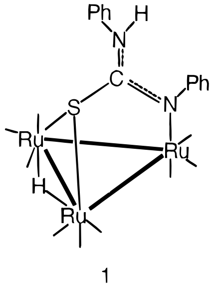
Reactions of the previously isolated trinuclear cluster (μ_2-H)Ru$_3$(CO)$_9$(μ_3,η^2-SCNHPhNPh) (**1**) with excess diphenylthiourea result in cluster fragmentation to produce the mononuclear complex Ru(CO)$_2$(η^2-SCNHPhNPh)$_2$ (**2**) containing two bidentate diphenylthioureato ligands. Room-temperature reactions of **1** with 1 or 2 equiv of triphenylphosphine result in substitution of one or two carbonyl groups, respectively, to give the clusters (μ_2-H)Ru$_3$(CO)$_8$-(PPh$_3$)(μ_3,η^2-SCNHPhNPh) (**3**) and (μ_2-H)Ru$_3$(CO)$_7$(PPh$_3$)$_2$(μ_3,η^2-SCNHPhNPh) (**4**). An X-ray crystal structure analysis shows **3** to represent a monosubstituted derivative of **1** with the PPh$_3$ ligand occupying an equatorial position on one of the two bridgehead ruthenium atoms; the crystal belongs to the triclinic space group $P\bar{1}$; $Z = 2$, $a = 10.014(2)$ Å, $b = 14.449(4)$ Å, $c = 14.573(4)$ Å, $\alpha = 100.38(2)°$, $\beta = 98.70(2)°$, and $\gamma = 107.20(2)°$. Thermolysis of either **1** in the presence of 2 equiv of PPh$_3$, or of **4** alone, gives the sulfur-capped, trinuclear cluster Ru$_3$(CO)$_7$(PPh$_3$)(μ_2,η^2-C$_6$H$_5$)(μ_2-PPh$_2$)(μ_3-S) (**5**). X-ray structural analysis of **5** shows a diphenylphosphido bridge and a phenyl bridge resulting from P−C bond activation of a PPh$_3$ group and C−H activation of the aryl group; crystals of **5** are monoclinic, space group $P2_1/n$; $Z = 4$, $a = 10.824(1)$ Å, $b = 19.193(5)$ Å, $c = 20.953(2)$ Å, and $\beta = 97.44(1)°$. Diphenylphosphinoethane (dppe) is found to replace two carbonyl ligands on two adjacent Ru atoms to give the cluster (μ_2-H)Ru$_3$(CO)$_7$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)- (μ_3,η^2-SCNHPhNPh) (**6**) whose X-ray structural analysis shows a dppe ligand bound *cis* to the μ_2-S of the diphenylthioureato ligand and *cis* to the μ_2-H ligand. Crystals of **6** are monoclinic, space group $P2_1/n$; $Z = 4$, $a = 17.667(7)$ Å, $b = 17.681(5)$ Å, $c = 18.049(4)$ Å, and $\beta = 108.06(2)°$.

Introduction

The reactions of thioureas SC(NR^{1}R^2)$_2$ with triruthenium dodecacarbonyl were first studied in this laboratory and produced a series of new and unique cluster complexes.[1] Trinuclear complexes of the type (μ_2-H)-(Ru$_3$(CO)$_9$(μ_3,η^2-RNCSNRH) were obtained from the reaction of Ru$_3$(CO)$_{12}$ with thiourea (R = H) and its dimethyl and diphenyl derivatives (R = Me, Ph).[1a] In the case of diethylthiourea, in addition to the analogous trinuclear cluster Ru$_3$(CO)$_9$(μ_2-H)(μ_3,η^2-EtNCSNHEt), the tetranuclear clusters Ru$_4$(CO)$_{8-n}$(μ_2-CO)$_3$(μ_4-S)$_2$-{C(NRH)}$_n$ (n = 1, 2) (R = Et) were isolated.[1b] With diisopropylthiourea, the sole products were tetranuclear clusters of the same type (R = i-Pr).[1c] In the reaction of Ru$_3$(CO)$_{12}$ with di-*tert*-butylthiourea, two complexes, Ru$_3$(CO)$_8$(μ_2-H)-(μ_3-S)(η^2-CH$_2$CMe$_2$NHCNHtBu) and Ru$_3$(CO)$_9$(μ_2-H){(μ_3-S)Ru(CO)$_3$(η^2-CH$_2$CMe$_2$NHCNHtBu)}, were isolated in which not only C−S bond breaking of the thiourea is observed but also C−H activation of one of the *tert*-butyl groups.[1d] Thus the nature of the thiourea substituent R has a strong influence on the type of cluster formed. This is most likely a result of stabilization of one of the tautomeric forms of the thiourea by the substituent R. Among the trinuclear clusters containing the thiourea ligands in a μ_3,η^2-face-capping mode, the cluster in which R = Ph, (μ_2-H)(Ru$_3$-(CO)$_9$(μ_3,η^2-SCNPhNPhH) (**1**) could be isolated in a relatively high yield (59%) and was found to be relatively stable toward air. Given that thioureas are of interest, owing to the proven catalytic activity of thio-



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† Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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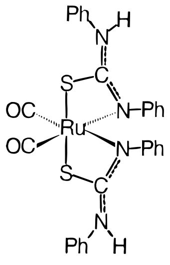
urea−palladium complexes,[2] and investigations of the substitution reactions of their cluster complexes can often provide useful information regarding intermediates as well as mechanistic details of homogeneous catalytic processes, a reactivity study of **1** was undertaken.

Results and Discussion

Reaction of $(\mu_2\text{-H})(Ru_3(CO)_9(\mu_3,\eta^2\text{-SCNPhNPhH})$ (1) with Excess Diphenylthiourea. Stirring a room-temperature THF solution of **1** with excess diphenylthiourea over an extended period (4 days) resulted in formation of the mononuclear species $Ru(CO)_2(SCNHPhNPh)_2$ (**2**) in 15.4% yield. This compound could also be produced in long-term reactions of $Ru_3(CO)_{12}$ with excess diphenylthiourea (yield 23.4%). The mononuclear complex **2** was isolated from the reaction mixture by TLC as a colorless band and could be recrystallized from mixed-solvent systems (CH_2Cl_2/hexane). IR and ^1H NMR data are consistent with a mononuclear system containing two intact diphenylthioureato ligands. The presence of an M^+ peak at 612 mass units in FAB mass spectra of **2** further support this assignment. An independently published, X-ray structural analysis of the Os analogue, $Os(CO)_2(pySH)_2$,[3] showed the CO ligands to occupy *cis* positions and the sulfur ligands to occupy *trans* positions on a central Os atom. The appearance of two bands in the ν_{CO} region of the IR spectrum of **2** indicates a species of C_2 symmetry requiring the two carbonyl ligands to be placed in a *cis* orientation. The valence requirements of the central Ru atom in **2** are fulfilled if the bidentate diphenylthioureato fragment is considered as a four-electron donor. This should result in decreased sp^2 character at the central C of the NCN portion of the ligand as compared to the trinuclear cluster **1** wherein the ligand serves as a five-electron donor. This aspect is supported by the observed low-energy shift of the ν_{NCN} stretch in IR spectra of **2** as well as a high-energy shift for ν_{NH}.



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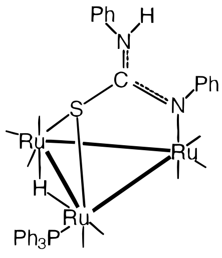
Mononuclear complexes analogous to **2** have also been isolated from reactions of $Ru_3(CO)_{12}$ and pyridine-2-thione (pySH), but in contrast to the diphenylthioureato derivative described here, vigorous conditions were required to produce the complex $Ru(CO)_2(\eta^2\text{-pySH})_2$.[4] An alternative synthesis was outlined for the pySH analogue of **2** involving reductive carbonylation of $RuCl_3\cdot nH_2O$. The chlorocarbonyl complex thus formed was then allowed to react with the thione. However, attempts at the same procedure to afford **2** were found to give very low yields. The postulated mechanism in the reaction with $RuCl_3\cdot nH_2O$ proposes a six-coordinate intermediate "$Ru(CO)_2(Cl)_2(pySH)_2$", wherein the pySH ligand is sulfur-bound and a proton resides on the ring nitrogen, that undergoes elimination of HCl via the chloride ligands *cis* to the pySH ligands to give the product. The less acidic nature of the NH protons of thiourea relative to the pyridinium proton is probably a contributing factor to the low yields obtained in similar reactions using diphenylthiourea. Furthermore, considering that formation of **2** occurs in better yields from reactions of $Ru_3(CO)_{12}$ as well as of **1** with excess diphenylthiourea, it follows that the trinuclear species **1** is a more productive precursor (as compared to the six-coordinate intermediate suggested above) in the formation of **2**.

Reactions of $(\mu_2\text{-H})Ru_3(CO)_9(\mu_3,\eta^2\text{-SCNHPhNPh})$ (1) with Triphenylphosphine. Stirring a THF solution of **1** with 1 or 2 equiv of PPh_3 over a period of 24 h resulted in substitution of one or two carbonyl groups to produce the 48-electron trinuclear clusters $(\mu_2\text{-H})Ru_3(CO)_8(PPh_3)(\mu_3,\eta^2\text{-SCNHPhNPh})$ (**3**) and $(\mu_2\text{-H})Ru_3(CO)_7(PPh_3)_2(\mu_3,\eta^2\text{-SCNHPhNPh})$ (**4**), respectively. If an excess of PPh_3 was used, no further substitution was observed. Clusters **3** and **4** could be separated from the reaction mixture using preparative TLC, eluting as two distinct orange bands. However, ^1H NMR spectroscopy of the products isolated from the plates showed the presence of **4** in samples of **3** and vice versa. Pure, crystalline samples of **3** could be obtained by crystallization from CH_2Cl_2/hexane solvent mixtures. Spectral data for the clusters **3** and **4**, as summarized in the Experimental Section, provide important information concerning the nature of the carbonyl substitutions taking place on cluster **1**. The upfield shifts of the phosphorus signals in ^{31}P NMR spectra of **3** and **4** indicate the phosphine ligand is bound to the metal through a σ-bond. This conclusion is also corroborated by the integrals of the ^1H NMR spectra, showing intact PPh_3 groups. The placement of the phosphine ligands on the cluster adjacent to the bridging hydride can be deduced from the presence of fine structure at the signals of the hydride ligands; a doublet is observed in spectra of **3** while a triplet is observed in spectra of **4**. Furthermore, the small values of the coupling constants indicate a *cis* orientation of the coupling groups.[5] From the presence of NH and NCN bands in solid-state IR spectra as well as the integrals of the ^1H NMR spectra in the phenyl region, it is clear that the diphenylthio-



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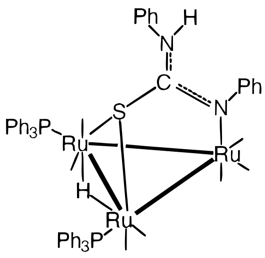

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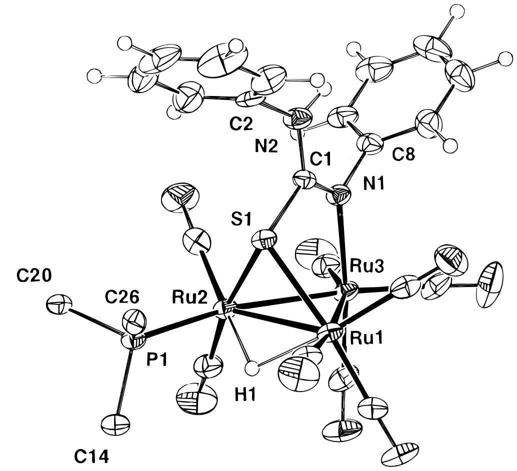


Figure 1. Molecular structure of **3**; only the *ipso*-carbon atoms of the PPh_3 ligand are shown.

ureato ligand is undisturbed by substitution at the metal skeleton. Cabeza *et al.* prepared several phosphine and phosphite derivatives of trinuclear clusters containing the 2-amino-6-methylpyridinato (ampy) capping ligand,[6] as well as the pyridine-2-thiol (pyS) ligand.[7] These reactions produced clusters similar to **3** and **4**; however, no monosubstituted derivatives were structurally characterized.

The structure of cluster **3** was determined by X-ray structural analysis. The molecule crystallizes in the triclinic crystal system, in the space group $P\bar{1}$ with two molecules per unit cell. The molecular structure of **3** is shown in Figure 1. Crystal data are collected in Table 1, Table 2 gives the atomic coordinates, and Table 3 gives selected bond distances and angles for **3**.

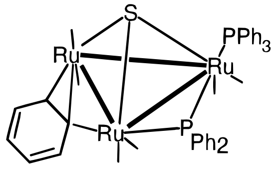
The triangular metal framework of cluster **3**, compared to that of **1,** is slightly perturbed by the presence of the PPh_3 ligand. In cluster **1** a mirror plane extends through Ru1 and the midpoint of the Ru2−Ru2′ bond, entailing equidistant Ru1−Ru2 and Ru1−Ru2′ bond lengths. Not only does the presence of the phosphine on only one side of the sulfur-bridged Ru−Ru bond destroy this symmetry, but it also renders all of the metal−metal bonds slightly unequal. Specifically, the non-sulfur-bridged bonds are shown to shorten, the shortest of which (Ru2−Ru3, 2.7642(10) Å) involves the Ru atom associated with the PPh_3 ligand. The Ru1−Ru2 bond elongates (Ru1−Ru2, 2.8592(11) Å in **3** vs 2.8421(5) Å in **1**). At the hydride ligand, the asymmetry manifests itself in a noticeably shorter bond between the hydride and the phosphine bonded Ru (Ru(1−H(1), 1.97(6) Å; Ru(2)−H(1), 1.69(6) Å). The atom H1 is found to fall 0.89(7) Å below the M_3 plane. Stated alternatively, the Ru1−H−Ru2 plane forms an angle of 51° with the M_3 plane. As implied by the ^1H NMR spectrum, the binding site of the PPh_3 is an equatorial position on one of the sulfur-bonded Ru atoms, *cis* to the bridging hydride.

Within the S−C−N base of the diphenylthioureato ligand, substitution at the metal framework has little effect; the bond distances and angles there remain essentially unchanged. However, the Ru3−N1 bond is approximately 0.02 Å shorter in **3** (Ru1−N1, 2.167(3) Å in **1** vs Ru3−N1, 2.149(5) Å in **3**). This shorter bond length does not change the Ru3−N1−C1 bond angle, nor does it influence the remaining structural features of the diphenylthioureato ligand.

In the formation of the disubstituted cluster **4**, the second PPh_3 ligand is assumed to coordinate to the second sulfur-bonded Ru atom. The structure of the disubstituted PPh_3 ampy cluster, $(\mu_2\text{-H})Ru_3(CO)_7(PPh)_2(\mu_3,\eta^2\text{-ampy})$, has been reported by Cabeza *et al.*[8] There the two phosphine groups occupy equatorial positions on the nitrogen-bridged Ru atoms. The infrared data given for the Cabeza cluster show a ν_{CO} structure analogous to that of **4** as well as $J_{(\mu\text{-H})-P}$ coupling constants of the same order (8.3 Hz) as those found in spectra of **4**. Based on these observations, the two clusters can be assumed isostructural.

Cabeza *et al.* also presented a trinuclear complex containing a μ_3,η^2-face-capping ligand derived from 2-mercaptobenzimidazolate (mbim) in which two carbonyl groups are substituted with PPh_3 ligands.[6a] Like the diphenylthioureato derivative, this compound was prepared via room-temperature reaction of the starting trinuclear cluster and PPh_3. However, the disubstituted mbim cluster proved impossible to separate from its monosubstituted counterpart and was therefore never fully characterized.

Refluxing a toluene solution of **1** with 2 equiv of PPh_3 produced the trinuclear cluster $Ru_3(CO)_7(\mu_2\text{-Ph})(\mu_2\text{-}PPh_2)(PPh_3)(\mu_3\text{-S})$ (**5**). Similar results were obtained from thermolysis reactions of **4**. The product could be separated from the reaction mixture as a red band on Al_2O_3 TLC plates. Refluxing solutions of the reactants in a lower boiling solvent (i.e., THF) over extended periods of time resulted in formation of **5** but only in very small quantities; the major product was the PPh_3-substituted cluster **3**. According to infrared and ^1H and ^{31}P NMR spectroscopic data (see Experimental Section), cluster **5** differs structurally from clusters **3** and **4**. The IR spectrum in the carbonyl region is simple, showing only four strong bands and indicating extensive substitution at the metal framework. The nature of these substitutions becomes more apparent upon considering the NMR spectra. In the ^1H NMR spectrum, a bridging hydride group is no longer observed and the number and nature of the phenyl groups has changed. The phenyl region is more complex than that observed for **1**. In addition, the characteristic IR stretches of the diphenylthioureato ligand are absent. The presence of



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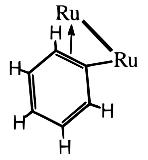

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Table 1. Crystallographic Data for 3, 5, and 6[a]

compound	**3**	**5**	**6**
mol formula	$C_{39}H_{26}N_2O_8PRu_3S$	$C_{42}H_{30}O_6P_2Ru_3S{\cdot}CH_2Cl_2$	$C_{46}H_{36}N_2O_7P_2Ru_3S_2(CH_2Cl_2)_2{\cdot}H_2O$
MW	1016.88	1112.8	1313.85
Z	2	4	4
cryst dimens/mm	0.34 × 0.27 × 0.23	0.68 × 0.53 × 0.42	0.99 × 0.65 × 0.61
cryst color/habit	orange/blocks	black/blocks	orange-red/blocks
cryst syst	triclinic	monoclinic	monclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	10.014(2)	10.824(1)	17.667(7)
b/Å	14.449(4)	19.193(5)	17.681(5)
c/Å	14.573(4)	20.953(2)	18.049(4)
α/deg	100.38(2)	90	90
β/deg	98.70(2)	97.44(1)	108.06(2)
γ/deg	107.20(2)	90	90
V/Å^3	1933.8(8)	4316.2(13)	5360(3)
D_c/g cm^{-3}	1.746	1.712	1.628
μ(Mo Kα)/mm^{-1}	2.56	1.329	1.184
T of data collctn (K)	193(1)	293(1)	203(1)
F(000)	2003.75	2200	2616
no. of unique data	6781	7595	9410
no. of. data used [$F_o > 2.5\sigma(F_o)$]	5278	7056	5111
$2\theta_{min}/2\theta_{max}$(deg)	3/50	3/50	3/55
absorptn correctn	empirical	semiemp/ψ scans	semiemp/ψ scans
max/min transmission	0.5936/0.4826	0.2756/0.1875	0.1715/0.1176
instrumental error factor k[b]	0.0005		
$R(R')$[c] (**3**)	0.036(0.055)		
$R(>2\sigma F^2)$/R1(all) (**5**, **6**)[d,e]		0.0506(0.0726)	0.0754(0.1526)
w$R2(>2\sigma F^2)$/w$R2$(all)[f]		0.1263 (0.1402)	0.1666(0.2044)
wa		0.0835	0.0964
resid el-density diff features (max, min)/e Å^{-3}	0.70, −0.55	1.247, −0.884	1.678, −1.133

[a] Details in common: data collected on a Stoe-Siemens AED 2 four-circle diffractometer; graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å; scan mode $\omega-\theta$. [b] Refinement was by full-matrix least squares with a weighting scheme of the form $w^{-1} = \sigma^2(F_o) + k(F_o^2)$. [c] Data refinement using NRCVAX, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R' = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. [d] Data refinement using SHELXL 93. [e] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [f] w$R2 = [\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^4]\}]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (\mathrm{wa}P)^2]$, $P = (F_o^2 + 2F_c^2)/3$.

a phosphido bridge is verified by the downfield shift of one of the two peaks found in ^{31}P NMR spectra of **5**.[9] The remaining peak occurs in the region normally assigned to σ-bonded PPh_3. On the basis of the coincidence of spectral data with the crystallographically characterized trinuclear cluster $Ru_3(CO)_6(\mu_2\text{-}Ph)(\mu_2\text{-}PPh_2)_2(\mu_3,\eta^2\text{-ampy})$,[6a] Cabeza identified a trinuclear cluster containing two diphenylphosphido bridges, a bridging aryl group, and a μ_3,η^2-methylbenzimidazole ligand [$Ru_3(CO)_6(\mu_2\text{-}C_6H_5)(\mu_2\text{-}PPh_2)_2(\mu_3,\eta^2\text{-mbim})$]. The agreement of the ν_{CO} region of IR spectra of **5** with this mbim-based cluster at first suggested a second structural anologue to the ampy cluster; however, ambiguities in the spectral and analytical data led to the crystallographic characterization of this species, confirming the molecular formula $Ru_3(CO)_7(\mu_2\text{-}\eta^2\text{-}C_6H_4)(\mu_2\text{-}PPh_2)(PPh_3)(\mu_3\text{-}S)$ (**5**).

Red, block crystals of **5** were found to crystallize in the monoclinic space group $P21/n$ with 4 molecules per unit cell. One molecule of dichloromethane was associated with each molecule of **5**. Relevant structural data for **5** are summarized in Table 1. The crystallographically determined structure of **5** is presented in Figure 2. The atomic coordinates and relevant bond lengths and angles for **5** are summarized in Tables 4 and 5, respectively.

The molecular structure of **5** shows the original trinuclear Ru framework where the only part of the diphenylthioureato ligand that remains is a capping μ_3-S. Further bridging ligands include a diphenylphosphido group spanning the Ru2−Ru3 bond and an aryl group wherein the C1 atom bridges the Ru1−Ru2 vector. One terminal PPh_3 ligand is bound to Ru1 while six terminal carbonyl groups complete the coordination spheres of the Ru atoms. Consistent with the ^{1}H NMR spectrum, no hydride ligands are present in the structure of **5**. Treating the μ_3-S as a four-electron donor, the μ_2-PPh_2 group as a three-electron donor, and the aryl group as a three-electron donor, cluster **5** contains a total of 48 electrons and is electronically saturated.

The ranges of metal−metal bond lengths are, on the average, consistent with single bonds (**5**, average Ru−Ru, 2.7706(7) Å); however, they have shortened relative to those of **1**. The Ru−S bonds show two typical Ru−S bond lengths and one rather short Ru−S distance (Ru3−S1, 2.365(2) Å). The bonding situation at the bridging aryl group is somewhat unusual and is illustrated with the associated bond lengths and atom orientations. The C1 bridge itself is asymmetric (Ru1−C1, 2.130(6) Å; Ru2−C1, 2.355(6) Å). The calculated distance between the C2 atom of the bridging aryl group and Ru2 indicates a bonding interaction (Ru2−C2, 2.542(7) Å). Since the presence of the phenyl hydrogen atom on C2 was verified in difference maps (and refined), the C2 atom, together with C1 most likely participate in a side-on π-interaction with Ru2 while the Ru1−C1 represents a σ-interaction. This σ,π-type interaction is also suggested by the tilting of the plane of the aryl group toward Ru2; the angle between the aryl plane and the Ru_3 plane is calculated as 67.97(14)°. Furthermore, the double bonds of the C_6H_5 ligand are localized between C3 and C4 (1.360(11) Å) and C5 and C6 (1.375(9) Å), while the remaining C−C bond lengths indicate single-bond character. The phosphido group bridges the Ru−Ru vector in a relatively symmetric manner.

In assuming a μ_2,η^2-bridging mode, the aryl group of **5** is somewhat unique. The compounds of Cabeza *et al.*

Table 2. Atomic Coordinates and B_{iso} (Å^2) for Refined Atoms of 3

	x	*y*	*z*	B_{iso}
Ru1	0.22446(6)	0.12269(4)	0.16974(4)	1.94(3)
Ru2	0.21500(6)	0.28756(4)	0.30735(4)	1.765(25)
Ru3	0.14197(6)	0.09788(4)	0.33881(4)	1.96(3)
S1	0.03900(17)	0.19799(13)	0.16148(12)	1.91(8)
P1	0.30529(18)	0.43234(14)	0.25007(13)	1.90(8)
N1	−0.0735(6)	0.0771(4)	0.2691(4)	2.0(3)
N2	−0.2375(6)	0.1111(4)	0.1594(4)	2.5(3)
C1	−0.1022(7)	0.1211(5)	0.2022(5)	1.8(3)
C2	−0.2715(7)	0.1742(6)	0.0991(5)	2.5(3)
C3	−0.2525(9)	0.2725(7)	0.1377(6)	3.9(4)
C4	−0.2875(10)	0.3315(7)	0.0804(8)	4.6(5)
C5	−0.3400(10)	0.2941(9)	−0.0141(9)	5.2(6)
C6	−0.3592(11)	0.1962(10)	−0.0536(7)	5.6(7)
C7	−0.3256(9)	0.1343(7)	0.0035(6)	3.8(5)
C8	−0.1933(7)	0.0157(5)	0.2995(5)	2.3(3)
C9	−0.2585(8)	−0.0834(6)	0.2520(6)	3.0(4)
C10	−0.3720(9)	−0.1427(6)	0.2818(7)	3.8(4)
C11	−0.4173(9)	−0.1032(7)	0.3602(7)	4.2(5)
C12	−0.3501(9)	−0.0043(7)	0.4086(6)	3.7(5)
C13	−0.2382(7)	0.0558(6)	0.3772(5)	2.7(4)
C14	0.5015(7)	0.4867(5)	0.2782(5)	2.1(3)
C15	0.5874(8)	0.4317(6)	0.3043(6)	2.9(4)
C16	0.7368(8)	0.4772(7)	0.3315(6)	3.7(4)
C17	0.7997(8)	0.5742(6)	0.3342(6)	3.3(4)
C18	0.7154(8)	0.6295(6)	0.3080(6)	3.5(4)
C19	0.5684(8)	0.5856(6)	0.2817(5)	2.8(4)
C20	0.2544(7)	0.5398(5)	0.2984(5)	2.2(3)
C21	0.2522(7)	0.5610(6)	0.3959(5)	2.6(4)
C22	0.2261(8)	0.6449(6)	0.4372(5)	2.8(4)
C23	0.1991(8)	0.7088(6)	0.3829(6)	3.3(4)
C24	0.1998(8)	0.6883(6)	0.2859(6)	3.1(4)
C25	0.2267(8)	0.6051(6)	0.2440(5)	2.7(4)
C26	0.2564(7)	0.4172(5)	0.1208(5)	2.2(3)
C27	0.3543(8)	0.4148(6)	0.0624(5)	2.8(4)
C28	0.3091(9)	0.3972(7)	−0.0359(6)	3.6(4)
C29	0.1681(10)	0.3814(7)	−0.0767(6)	4.0(5)
C30	0.0692(8)	0.3816(6)	−0.0196(6)	3.5(4)
C31	0.1134(8)	0.3993(6)	0.0789(5)	2.7(4)
C32	0.0975(8)	−0.0106(6)	0.1206(5)	2.8(4)
O32	0.0229(6)	−0.0902(5)	0.0908(4)	4.1(3)
C33	0.2776(8)	0.1574(6)	0.0537(5)	2.7(4)
O33	0.3116(6)	0.1698(5)	−0.0154(4)	4.5(3)
C34	0.3812(8)	0.0797(6)	0.2006(5)	2.7(4)
O34	0.4766(6)	0.0523(5)	0.2164(4)	3.8(3)
C35	0.1009(8)	0.1293(6)	0.4629(6)	2.7(4)
O35	0.0853(6)	0.1477(5)	0.5388(4)	4.3(3)
C36	0.1012(8)	−0.0443(7)	0.3210(6)	3.0(4)
O36	0.0815(8)	−0.1269(5)	0.3091(5)	5.4(4)
C37	0.3379(8)	0.1297(6)	0.3915(5)	2.8(4)
O37	0.4562(6)	0.1492(5)	0.4256(4)	4.0(3)
C38	0.0800(8)	0.3170(6)	0.3715(5)	2.6(3)
O38	−0.0084(6)	0.3324(5)	0.4074(4)	4.3(3)
C39	0.3545(8)	0.3380(6)	0.4212(5)	2.6(4)
O39	0.4361(6)	0.3701(5)	0.4927(4)	4.3(3)
H1	0.333(7)	0.259(5)	0.245(5)	2.5(15

mentioned above[6a] are the first examples of symmetrical bridging phenyl groups across Ru−Ru bonds. Other platinum group clusters with η^1-phenyl groups are also known.[10] As for a σ,π-interaction of a vinyl ligand, the ampy bridged cluster of Cabeza has been shown to add diphenylacetylene in such a way that the resulting alkenyl ligand employs a σ,π -interaction in bridging a Ru−Ru bond, similar to the situation for **5**.[11] With respect to phenyl rings serving as ligands, this type of interaction has been observed only once in a trinuclear cluster consisting of Mo, Rh, and Pt.[12] However, the σ,π-interaction exhibited in cluster **5** represents the first example of an aryl ligand employing combined bridging and side-on π-coordination in a ruthenium cluster.

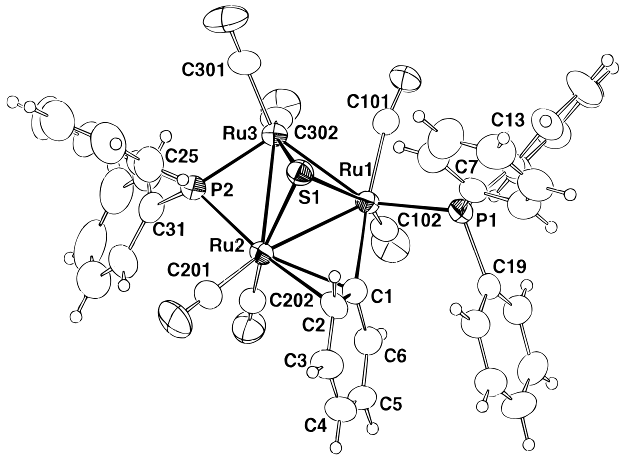

Figure 2. Molecular structure of **5**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3

Bond Distances

Ru(1)−Ru(2)	2.8592(11)	Ru(3)−C(36)	1.933(9)
Ru(1)−Ru(3)	2.7642(10)	P(1)−C(14)	1.836(7)
Ru(1)−S(1)	2.4128(17)	P(1)−C(20)	1.830(7)
Ru(1)−H(1)	1.97(6)	P(1)−C(26)	1.830(7)
Ru(2)−Ru(3)	2.7614(11)	S(1)−C(1)	1.775(6)
Ru(2)−P(1)	2.3726(19)	N(1)−C(1)	1.298(8)
Ru(2)−S(1)	2.4138(20)	N(1)−C(8)	1.448(8)
Ru(2)−H(1)	1.69(6)	N(2)−C(1)	1.357(8)
Ru(3)−N(1)	2.149(5)	N(2)−C(2)	1.451(9)

Bond Angles

Ru(1)−Ru(2)−Ru(3)	58.89(3)	Ru(3)−N(1)−C(1)	122.6(4)
Ru(1)−Ru(2)−P(1)	106.81(5)	Ru(3)−N(1)−C(8)	120.0(4)
Ru(1)−Ru(3)−Ru(2)	62.32(3)	S(1)−Ru(2)−P(1)	94.16(7)
Ru(1)−S(1)−Ru(2)	72.65(5)	S(1)−C(1)−N(1)	120.0(5)
Ru(1)−S(1)−C(1)	106.16(22)	S(1)−C(1)−N(2)	116.6(5)
Ru(1)−H(1)−Ru(2)	102(3)	N(1)−C(1)−N(2)	123.3(6)
Ru(2)−Ru(1)−Ru(3)	58.79(3)	C(1)−N(1)−C(8)	117.4(5)
Ru(2)−P(1)−C(14)	114.51(23)	C(1)−N(2)−C(2)	123.8(6)
Ru(2)−P(1)−C(20)	116.03(23)	C(14)−P(1)−C(20)	101.5(3)
Ru(2)−P(1)−C(26)	116.08(23)	C(14)−P(1)−C(26)	103.7(3)
Ru(2)−S(1)−C(1)	103.00(22)	C(20)−P(1)−C(26)	103.2(3)

The formation of **5** from thermolysis reactions of **1** in the presence of PPh$_3$ has interesting implications. The thermolysis of **1** in the absence of PPh$_3$ leads to an entirely different group of products.[13] This, in conjunction with formation of **5** in thermolysis reactions of **4**, suggests the intermediacy of a PPh$_3$-substituted derivative. The degradation of PPh$_3$ groups to give phosphido bridges is not unfounded, and their formation in the presence of a bridging hydride to provide for elimination of benzene also occurs.[14] The mechanism for the formation of the η^2-aryl ligand in **5** has not been firmly established but presumably results from orthometalation of one of the PPh$_3$ groups of **4** formed *in situ* which, rather than eliminating benzene, forms the bridging aryl group. Elimination of a diaminocarbene fragment from the diphenylthioureato ligand may be responsible for the absence of the hydride, implying priority to the P−C bond activation.

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Table 4. Atomic Coordinates($\times 10^4$) and U_{eq} ($\times 10^3$) (Å^2) for Refined Atoms of 5

	x	*y*	*z*	*U*(eq)
Ru(1)	1243(1)	1654(1)	4450(1)	32(1)
Ru(2)	2499(1)	2488(1)	5403(1)	33(1)
Ru(3)	−137(1)	2400(1)	5193(1)	36(1)
S(1)	1131(2)	2923(1)	4489(1)	38(1)
P(1)	1547(1)	1267(1)	3402(1)	34(1)
P(2)	1059(2)	2920(1)	6011(1)	37(1)
C(1)	3218(6)	1742(3)	4638(3)	40(2)
C(2)	3849(6)	2359(4)	4504(3)	41(2)
C(3)	5163(7)	2416(4)	4613(4)	56(2)
C(4)	5862(7)	1860(5)	4843(4)	63(2)
C(5)	5288(6)	1232(4)	4972(3)	53(2)
C(6)	4011(6)	1175(4)	4885(3)	48(2)
C(7)	1538(6)	1905(4)	2756(3)	40(2)
C(8)	1071(8)	2572(4)	2816(4)	57(2)
C(9)	1000(9)	3025(4)	2309(4)	73(3)
C(10)	1366(8)	2845(5)	1738(4)	69(2)
C(11)	1840(7)	2194(5)	1668(4)	62(2)
C(12)	1930(7)	1726(4)	2174(3)	52(2)
C(13)	341(6)	647(3)	3068(3)	39(2)
C(14)	−376(7)	758(4)	2476(3)	55(2)
C(15)	−1339(8)	301(5)	2257(4)	72(2)
C(16)	−1589(7)	−265(4)	2616(4)	62(2)
C(17)	−878(7)	−381(4)	3199(4)	58(2)
C(18)	61(6)	70(3)	3424(3)	48(2)
C(19)	3046(6)	827(3)	3370(3)	36(1)
C(20)	3225(6)	123(4)	3485(3)	46(2)
C(21)	4392(8)	−175(4)	3527(4)	59(2)
C(22)	5423(7)	243(4)	3453(4)	60(2)
C(23)	5252(6)	942(4)	3335(3)	50(2)
C(24)	4086(6)	1237(4)	3299(3)	43(2)
C(25)	911(6)	3859(3)	6095(3)	44(2)
C(26)	362(8)	4133(4)	6601(4)	64(2)
C(27)	193(11)	4850(5)	6648(5)	94(3)
C(28)	572(10)	5299(5)	6187(5)	88(3)
C(29)	1083(9)	5021(4)	5688(5)	77(3)
C(30)	1261(7)	4312(4)	5635(4)	58(2)
C(31)	1148(7)	2611(3)	6836(3)	45(2)
C(32)	2270(8)	2663(4)	7241(3)	59(2)
C(33)	2399(10)	2399(5)	7852(4)	82(3)
C(34)	1429(13)	2099(5)	8089(4)	93(4)
C(35)	290(11)	2054(5)	7712(4)	79(3)
C(36)	164(8)	2304(4)	7084(4)	59(2)
C(101)	−554(6)	1525(4)	4213(3)	45(2)
O(101)	−1538(4)	1371(3)	4013(3)	71(2)
C(102)	1336(6)	776(4)	4852(3)	44(2)
O(102)	1367(5)	263(3)	5134(3)	69(2)
C(201)	3670(6)	3200(4)	5683(3)	44(2)
O(201)	4357(5)	3622(3)	5869(3)	73(2)
C(202)	3090(6)	1820(4)	6044(3)	44(2)
O(202)	3397(5)	1403(3)	6410(3)	60(1)
C(301)	−1461(6)	3034(4)	5121(3)	46(2)
O(301)	−2252(5)	3429(3)	5065(3)	76(2)
C(302)	−918(6)	1711(4)	5644(3)	47(2)
O(302)	−1444(5)	1287(3)	5875(3)	70(2)
Cl(1)	4875(17)	4412(6)	4309(5)	476(9)
Cl(2)	3065(8)	4406(6)	3365(7)	410(7)
C(1S)	3579(26)	4959(12)	4030(12)	366(24)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5

Bond Distances

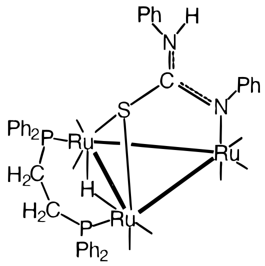
Ru(1)−Ru(2)	2.7738(8)	P(1)−C(7)	1.825(7)
Ru(1)−Ru(3)	2.7032(7)	P(1)−C(13)	1.836(6)
Ru(1)−P(1)	2.381(2)	P(1)−C(19)	1.838(6)
Ru(1)−S(1)	2.441(2)	P(2)−C(25)	1.820(7)
Ru(1)−C(1)	2.130(6)	P(2)−C(31)	1.818(7)
Ru(2)−Ru(3)	2.8348(7)	C(1)−C(2)	1.415(9)
Ru(2)−P(2)	2.292(2)	C(1)−C(6)	1.440(9)
Ru(2)−S(1)	2.413(2)	C(2)−C(3)	1.414(10)
Ru(2)−C(1)	2.355(6)	C(3)−C(4)	1.360(11)
Ru(2)−C(2)	2.542(7)	C(4)−C(5)	1.398(11)
Ru(3)−P(2)	2.243(2)	C(5)−C(6)	1.375(9)
Ru(3)−S(1)	2.365(2)		

Bond Angles

Ru(1)−Ru(2)−Ru(3)	57.62(2)	P(2)−Ru(2)−C(1)	155.0(2)
Ru(1)−Ru(3)−Ru(2)	60.06(2)	P(2)−Ru(2)−C(2)	160.9(2)
Ru(1)−C(1)−Ru(2)	76.2(2)	C(1)−Ru(1)−Ru(3)	117.9(2)
Ru(2)−S(1)−Ru(1)	69.70(5)	C(1)−Ru(1)−S(1)	88.1(2)
Ru(2)−C(2)−H(2)	98(4)	C(1)−Ru(2)−C(2)	33.3(2)
Ru(3)−Ru(1)−Ru(2)	62.32(2)	C(1)−C(2)−Ru(2)	66.1(3)
Ru(3)−P(2)−Ru(2)	77.37(5)	C(1)−C(2)−H(2)	122(4)
Ru(3)−S(1)−Ru(1)	68.43(5)	C(2)−C(1)−Ru(1)	122.0(5)
Ru(3)−S(1)−Ru(2)	72.77(5)	C(2)−C(1)−Ru(2)	80.6(4)
P(1)−Ru(1)−Ru(2)	136.93(4)	C(2)−C(1)−C(6)	115.0(6)
P(1)−Ru(1)−Ru(3)	148.12(4)	C(3)−C(2)−C(1)	122.3(7)
P(1)−Ru(1)−S(1)	110.82(6)	C(3)−C(2)−H(2)	113(4)
P(2)−Ru(2)−S(1)	85.66(6)	C(31)−P(2)−C(25)	103.1(3)

Both the ampy and mbim PPh$_3$ clusters of Cabeza underwent thermal activation of P−C bonds to form η^1-phenyl-bridged species. The disubstituted ampy clusters required high temperatures and the presence of H$_2$ to initiate P−C bond cleavage while for the mbim clusters, refluxing a THF solution of the unsubstituted species in the presence of 2 equiv of PPh$_3$ gave a product analogous to the ampy−aryl cluster. Cluster **1** shows reactivity toward P−C bond activation intermediate between that of the ampy and the mbim clusters in that thermal activation is necessary but the presence of H$_2$ is not required.

Reactions of (μ_2-H)Ru$_3$(CO)$_9$(μ_3,η^2-SCNHPhNPh) (1) with Diphenylphosphinoethane (dppe). Complex **1** reacts almost instantaneously with the difunctional phosphine diphenylphosphinoethane (dppe) to give the trinuclear cluster (μ_2-H)Ru$_3$(CO)$_7$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(μ_3,η^2-SCNHPhNPh) (**6**) in high yield (80%). Cluster **6** could only be isolated by crystallization from the reaction solution; attempts to purify the compound with preparative TLC resulted in almost complete decomposition. The IR spectrum of **6** compares well with that of the disubstituted PPh$_3$ cluster **4**, and the presence of only a single peak in ^{31}P NMR spectra indicates a symmetrically bound dppe moiety. Combined, these spectroscopic features suggest substitution of a single carbonyl group on each of two adjacent Ru atoms. The most likely binding site of the dppe is bridging the two sulfur-bound Ru atoms, a condition that would allow for retention of the mirror-plane symmetry of **1**. The triplet displayed by the bridging hydride in the ^{1}H NMR spectrum confirms this placement, and the small coupling constant of that multiplet further implies a hydride *cis* to the two phosphorus atoms. An intact diphenylthioureato ligand is inferred from its characteristic bands in the IR spectra. The doublet observed in the alkyl region of the ^{1}H NMR spectrum of **6**, which originates from the ethylene grouping of the dppe ligand, suggests either perfectly equivalent CH$_2$ groups or a certain degree of fluxionality. In contrast, a triplet is observed in ^{1}H NMR spectra of the unligated dppe.



6

Because no analogous structure was found in the literature, a single-crystal X-ray structural analysis of

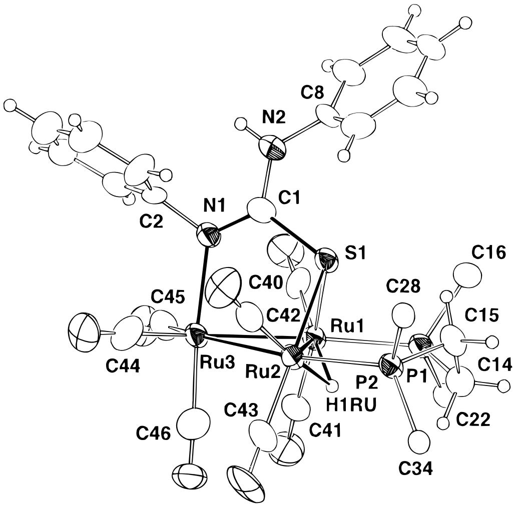


Figure 3. Molecular structure of **6**.

6 was undertaken. Crystals of **6** are monoclinic and belong to the space group $P2_1/n$ with four molecules per unit cell. Other relevant crystal data are collected in Table 1. The molecular structure of **6** is presented in Figure 3, and atomic coordinates and selected bond distances and angles are presented in Tables 6 and 7, respectively.

Figure 3 shows a trinuclear cluster similar to **1** except that substitution of two carbonyl ligands on adjacent Ru atoms has occurred and those coordination sites taken up in σ-bonds to the two P atoms of dppe. The Ru−P bond lengths observed in **6** are typical for this ligand in Ru clusters. As suggested by the spectroscopic data, the dppe ligand is found spanning the S-bridged edge of the trinuclear cluster in a position *cis* to the bridging hydride and the bridging sulfur. In contrast to the changes in Ru−Ru bond lengths brought on by substitution with a single PPh_3, the Ru−Ru bonds of the cluster are little changed by the presence of the dppe. The three Ru atoms and the two P atoms of the dppe ligand form a pentagonal base which is planar to within 0.053(1) Å. The bridging hydride (H1Ru) assumes a position 0.75(7) Å below the M_3P_2 plane while C14 and C15 are positioned respectively, 0.53(1) Å below and 0.49(1) Å above. Within the standard deviations of the determined bond lengths and angles, no changes for the diphenylthioureato ligand are observed.

A pseudomirror plane containing Ru3, N1, C1, and S1 bisects the Ru1−Ru2 and C14−C15 bonds. In the solid state, the dppe ligand distorts this symmetry element through the inequivalency of the methylene groups. However, the presence of only a doublet in the ^1H NMR spectrum indicates that these groups must be considerably fluxional in solution. No symmetry restraints are presented by the phenyl groups of the ligated dppe. Those groups are forced to adopt a single orientation with respect to the metal cluster, which renders them equivalent.

Two molecules of CH_2Cl_2 and one molecule of H_2O were found to cocrystallize in the unit cell. The CH_2Cl_2 originates from the crystallization solvent (CH_2Cl_2/hexanes), while the source of the molecule of H_2O is not sure.

Table 6. Atomic Coordinates ($\times10^4$) and U_{eq} ($\times10^3$) (Å^2) for Refined Atoms of 6

	x	*y*	*z*	*U*(eq)
Ru(1)	−374(1)	3762(1)	3066(1)	30(1)
Ru(2)	900(1)	3309(1)	2514(1)	31(1)
Ru(3)	895(1)	2923(1)	3994(1)	32(1)
P(1)	−1231(2)	4443(2)	2016(2)	32(1)
P(2)	574(2)	3880(2)	1277(2)	31(1)
S(1)	729(2)	4544(2)	3014(2)	31(1)
N(1)	1519(6)	3979(5)	4405(5)	36(2)
N(2)	1690(6)	5272(5)	4249(6)	41(3)
C(1)	1391(7)	4583(7)	3990(6)	35(3)
C(2)	2151(7)	3985(6)	5153(6)	31(3)
C(3)	2927(7)	4079(8)	5168(7)	47(3)
C(4)	3535(8)	4026(8)	5866(8)	57(4)
C(5)	3357(9)	3890(8)	6546(8)	58(4)
C(7)	1974(8)	3878(6)	5836(7)	39(3)
C(6)	2592(9)	3807(7)	6528(7)	54(4)
C(8)	1611(7)	5971(6)	3828(7)	36(3)
C(9)	1316(8)	6585(7)	4100(7)	46(3)
C(10)	1274(8)	7264(7)	3743(8)	52(4)
C(11)	1548(9)	7355(7)	3114(8)	54(4)
C(12)	1839(8)	6732(8)	2831(8)	54(4)
C(13)	1876(8)	6035(8)	3191(7)	50(4)
C(14)	−1041(7)	4308(7)	1073(6)	41(3)
C(15)	−197(7)	4610(7)	1082(6)	39(3)
C(16)	−1280(7)	5475(7)	2057(6)	33(3)
C(17)	−822(8)	5882(7)	2699(7)	42(3)
C(18)	−895(8)	6674(7)	2731(7)	42(3)
C(19)	−1430(8)	7040(7)	2120(8)	46(3)
C(20)	−1888(9)	6658(7)	1474(8)	53(4)
C(21)	−1807(7)	5876(7)	1449(7)	42(3)
C(22)	−2274(7)	4175(6)	1805(6)	34(3)
C(23)	−2558(10)	3500(9)	1421(9)	69(5)
C(24)	−3337(10)	3290(11)	1294(9)	80(5)
C(25)	−3845(9)	3683(9)	1540(8)	61(4)
C(26)	−3559(9)	4313(9)	1967(11)	77(5)
C(27)	−2779(9)	4553(9)	2089(9)	73(5)
C(29)	1460(9)	5170(7)	1158(7)	49(4)
C(28)	1400(7)	4405(7)	1129(6)	36(3)
C(30)	2110(10)	5542(8)	1070(8)	62(4)
C(31)	2725(9)	5151(9)	973(8)	59(4)
C(32)	2688(9)	4356(10)	938(8)	61(4)
C(33)	2025(7)	3982(8)	1022(8)	48(3)
C(34)	212(7)	3303(6)	408(6)	29(3)
C(35)	354(7)	3493(7)	−302(6)	38(3)
C(36)	−4(8)	3094(7)	−972(7)	47(3)
C(37)	−490(8)	2500(8)	−971(7)	48(3)
C(38)	−666(8)	2292(8)	−294(8)	54(4)
C(39)	−277(8)	2709(7)	387(7)	43(3)
C(40)	−593(7)	4249(7)	3894(6)	36(3)
O(40)	−727(6)	4515(5)	4427(5)	57(3)
C(41)	−1091(8)	2994(7)	3069(7)	43(3)
O(41)	−1556(6)	2546(6)	3073(6)	64(3)
C(42)	1992(9)	3351(7)	2872(7)	45(3)
O(42)	2696(5)	3420(6)	3111(5)	62(3)
C(43)	931(8)	2305(7)	2183(8)	48(3)
O(43)	957(7)	1690(5)	1962(6)	79(4)
C(44)	1884(8)	2413(8)	4417(7)	47(3)
O(44)	2482(6)	2094(6)	4678(5)	61(3)
C(45)	408(7)	2863(7)	4781(7)	40(3)
O(45)	61(5)	2762(6)	5228(5)	58(3)
C(46)	371(8)	2036(8)	3517(7)	48(3)
O(46)	75(7)	1494(5)	3251(5)	69(3)
C(1S)	3627(14)	6278(15)	5691(13)	144(9)
Cl(1S)	2810(3)	6155(3)	5948(3)	107(2)
Cl(2S)	3540(4)	6553(7)	4811(4)	219(5)
C(2S)	−5997(14)	4805(11)	2915(10)	118(8)
Cl(3S)	−5368(4)	4302(4)	2547(4)	138(2)
Cl(4S)	−5675(4)	4807(4)	3934(4)	130(2)
O(1W)	−5541(19)	4601(22)	−49(16)	366(27)
H(1RU)	−127(18)	3358(52)	2259(28)	33(29)

The dppe ligand typically takes on a bridging mode in cluster complexes and in doing so lends a degree of stability to the resulting cluster molecule.[15] This was the case with the trinuclear cluster (μ_2-H)$Ru_3(CO)_7(Ph_2PCH_2PPh_2)$($\mu_3$,$\eta^2$-ampy) prepared, but not structurally

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[15] Braunstein, P. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; VCH Publishers Inc.: New York, 1992; p 78.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 6

Bond Lengths

Ru(1)−Ru(2)	2.843(2)	P(1)−C(16)	1.828(12)
Ru(1)−Ru(3)	2.776(2)	P(1)−C(22)	1.826(12)
Ru(1)−P(1)	2.357(3)	P(2)−C(15)	1.830(12)
Ru(1)−S(1)	2.413(3)	P(2)−C(28)	1.817(12)
Ru(1)−H(1RU)	1.79(3)	P(2)−C(34)	1.812(11)
Ru(2)−Ru(3)	2.7601(13)	S(1)−C(1)	1.788(12)
Ru(2)−P(2)	2.353(3)	N(1)−C(1)	1.284(14)
Ru(2)−S(1)	2.417(3)	N(1)−C(2)	1.460(14)
Ru(2)−H(1RU)	1.73(3)	N(2)−C(1)	1.353(14)
Ru(3)−N(1)	2.178(9)	N(2)−C(8)	1.435(14)
P(1)−C(14)	1.848(10)	C(14)−C(15)	1.58(2)

Bond Angles

Ru(1)−S(1)−Ru(2)	72.13(9)	C(14)−P(1)−Ru(1)	114.8(4)
Ru(2)−Ru(3)−Ru(1)	61.80(4)	C(14)−C(15)−P(2)	114.1(8)
Ru(3)−Ru(1)−Ru(2)	58.82(4)	C(15)−P(2)−Ru(2)	115.7(4)
Ru(3)−Ru(2)−Ru(1)	59.38(4)	C(15)−C(14)−P(1)	112.8(8)
P(1)−Ru(1)−S(1)	90.08(11)	C(16)−P(1)−Ru(1)	120.3(4)
P(2)−Ru(2)−S(1)	86.88(10)	C(16)−P(1)−C(14)	101.0(5)
N(1)−C(1)−S(1)	119.1(9)	C(22)−P(1)−C(14)	103.5(5)
N(1)−C(1)−N(2)	124.7(11)	C(22)−P(1)−Ru(1)	113.0(4)
N(2)−C(1)−S(1)	116.2(9)	C(22)−P(1)−C(16)	102.1(5)
C(1)−S(1)−Ru(1)	105.9(4)	C(28)−P(2)−Ru(2)	112.8(4)
C(1)−S(1)−Ru(2)	106.5(4)	C(28)−P(2)−C(15)	101.3(5)
C(1)−N(1)−Ru(3)	122.4(8)	C(34)−P(2)−Ru(2)	119.7(4)
C(1)−N(1)−C(2)	118.6(10)	C(34)−P(2)−C(15)	100.9(5)
C(1)−N(2)−C(8)	129.0(10)	C(34)−P(2)−C(28)	104.2(5)
C(2)−N(1)−Ru(3)	118.8(7)		

characterized, by Cabeza and co-workers.[16] Contrary to thermolysis of the disubstituted PPh_3 analogue (recall thermolysis under H_2 pressure produced P−C bond cleavage), exposure of the dppe/ampy cluster to elevated temperatures had no effect. The stabilizing effect of the dppe ligand is apparent. The behavior of cluster **6** under thermolytic conditions, however, does not suggest a significant stabilization effect from the dppe ligand. Refluxing a cyclohexane solution of **6** over a period of 1 h resulted in formation of at least five different carbonyl clusters.

Conclusions

The added structural stability, originally perceived as possible with the face-capping diphenylthioureato ligand, has not always been shown to be the case. Exposure to certain reagents has produced cluster fragmentation even under extremely mild conditions, although it is noted that the diphenylthioureato ligand itself remains intact during this transformation. Other reagents, the phosphine-based reagents specifically, result in substitution of CO groups. While the phosphine-substituted derivatives of **1** undergo ligand transformations upon exposure to high temperatures, the original cluster nuclearity is maintained.

Experimental Section

Manipulations were carried out using standard Schlenk techniques under an N_2 atmosphere. Thermolysis reactions were performed in a high-pressure Schlenk tube able to withstand 8 bar of internal pressure. TLC plates were prepared by placing a uniform 0.5 mm layer of the appropriate support (Al_2O_3 or SiO_2; G or G/UV$_{254}$, Macherey-Nagel) on 20 × 20 cm glass plates. Laboratory solvents were purified and dried according to standard laboratory practices.[17] Distillation of solvents was carried out under an N_2 atmosphere; the inert atmosphere over the solvent was maintained thereafter. The cluster (μ_2-H)Ru$_3$(CO)$_9$- (μ_3,η^2-SCNHPhNPh) (**1**) was prepared according to a previously published procedure.[1a] Other chemicals (N,N′-diphenylthiourea (Fluka, 98%), triphenylphosphine (Merck, 98%), 1,2-bis(diphenylphosphino)ethane (Aldrich, 97%)) were purchased from the appropriate vendors and used as received. Infrared spectra were obtained using a Perkin-Elmer 1720 X spectrometer; ^{1}H, ^{13}C, and ^{31}P NMR spectra were acquired with either a Bruker AMX 400 or a Varian Gemini 200 BB spectrometer and the measurement temperature indicated. Elemental analyses were performed by the Mikroelementaranalytisches Laboratorium ETH, Zurich, Switzerland. FAB mass spectra were measured by Professor T. A. Jenny of the University of Fribourg, Fribourg, Switzerland, using 3-nitrobenzyl alcohol (NBA) as the matrix.

X-ray structural data were collected on a Stoe-Siemens AED 2 four-circle diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Low-temperature measurements were carried out using controlled-temperature nitrogen gas flow. Crystal structure data were solved with SHELXS-86[18] and refined with SHELXL-93[19] or the NRCVAX[20] program packages of the VAX-Cluster of the Départment de Calcul of the Université de Neuchâtel. Illustrations showing thermal motion ellipsoids were drawn using either the PLATON[21] or ZORTEP[22] program. Additional data for structures have been deposited with the Cambridge Crystallographic Data Centre, Union Road, GB-Cambridge CB2 1EW, U.K.

Synthesis of Ru(CO)$_2$(η^2-SCNHPhNPh)$_2$ (2) (a) Direct Synthesis. A solution of $Ru_3(CO)_{12}$ (40.5 mg, 0.0633 mmol) and $(PhNH)_2CS$ (86.4 mg, 0.39 mmol) in THF (20 mL) was stirred at room temperature for 7 days. The solvent was removed and the residue redissolved in CH_2Cl_2 and chromatographed on Al_2O_3 TLC plates in 1:1 CH_2Cl_2/cyclohexane, yielding in order of elution, **2** (26.6 mg, 23%) as a colorless band (detected with a UV lamp) and **1** (5.6 mg, 11.3%) as an orange band.

(b) Reaction of 1 with (PhNH)$_2$CS. A solution of **1** (36.2 mg, 0.046 mmol) and $(PhNH)_2CS$ (13.2 mg, 0.058 mmol) in THF (20 mL) was stirred at room temperature for 4 days. After the solvent was removed, **2** was isolated as a colorless band by TLC (Al_2O_3, 1:1 CH_2Cl_2/cyclohexane) (13.1 mg, 15.4%): IR (c-hex, 298 K) ν_{CO} (cm^{-1}) 2039 s, 1973 s; IR (KBr) ν_{NH} (cm^{-1}) 3360 m, ν_{NCN} (cm^{-1}) 1549 m; ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz) δ (ppm) 8.6 (s, br, 1H), 7.5−7.0 (m, 10H); FAB-MS (NBA) M$^+$ = 612. Anal. Calcd for $C_{28}H_{22}N_4O_2RuS_2 \cdot 0.25CH_2Cl_2$ (632.9): C, 53.6; H, 3.58; N, 8.85. Found: C, 53.84; H, 3.58; N, 8.90.

Synthesis of (μ_2-H)Ru$_3$(CO)$_8$(PPh$_3$)(μ_3,η^2-SCNHPhNPh) (3). A solution of **1** (78.4 mg, 0.100 mmol) and PPh_3 (27.6 mg, 0.105 mmol) in THF (20 mL) was stirred at room temperature for 24 h. The solvent was removed and the residue dissolved in CH_2Cl_2 and chromatographed on TLC plates (Al_2O_3, CH_2Cl_2/cyclohexane 30:70). Two major bands eluted. The first band contained compound **4** (trace). The second band was primarily compound **3** (69.9 mg, 69%) slightly contaminated with **4**. Orange-block crystals of **3** were obtained from CH_2Cl_2 solutions at room temperature: IR (c-hex, 298 K) ν_{CO} (cm^{-1}) 2064 m, 2029 vs, 1998 ms, 1979 m, 1970 m, 1946 w,sh; IR (KBr) ν_{NH} (cm^{-1}) 3354 wm, ν_{NCN} (cm^{-1}) 1572 m; ^{1}H NMR ($CDCl_3$, 298 K, 200 MHz) δ (ppm) 7.50−6.90 (m, 25H), 6.08 (s, br, 1H), −12.52 (d, J = 14 Hz, 1H); ^{31}P NMR($CDCl_3$, 298

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K, 200 MHz) δ (ppm) 25.9 (s). Anal. Calcd for $C_{39}H_{27}N_2O_8Ru_3PS$ (1018): C, 46.0; H, 2.67; N, 2.75. Found: C, 45.7; H, 2.78; N, 2.46.

Synthesis of (μ_2-H)Ru$_3$(CO)$_7$(PPh$_3$)$_2$(μ_3,η^2-SCNHPhNPh) (4). A solution of $Ru_3(CO)_{12}$ (50.0 mg, 0.064 mmol) and PPh_3 (35.2 mg, 0.134 mmol) in THF (20 mL) was stirred at room temperature for 24 h. The solvent was removed and the residue dissolved in CH_2Cl_2 and chromatographed on TLC plates (Al_2O_3, 30:70 CH_2Cl_2/cyclohexane). Only one major band migrated and consisted primarily of **4** (27mg, 34%) with traces of **3**: IR (c-hex, 298 K) ν_{CO} (cm^{-1}) 2042 vs, 1996 s, 1986 w, 1970 s, 1936 m; IR (KBr) ν_{NH} (cm^{-1}) 3366 wm, ν_{NCN} (cm^{-1}) 1571 m; ^{1}H NMR ($CDCl_3$, 298 K, 200 MHz) δ (ppm) 7.60−6.70 (m, 40H), 5.90 (s, br, 1H), −12.10 (t, J = 9 Hz, 1H); ^{31}P NMR ($CDCl_3$, 298 K, 200 MHz) δ (ppm) 29.0 (s). It was not possible to obtain a pure sample of **4**; a trace amount of **3** was persistently present; therefore, no elemental analysis was carried out on **4**. However, FAB-mass spectral analysis (in NBA) of a relatively pure sample shows an M$^+$ peak at 1253 mass units.

Synthesis of Ru$_3$(CO)$_7$(μ_2,η^2-C$_6$H$_4$)(μ_2-PPh$_2$)(PPh$_3$)(μ_3-S) (5). A solution of **1** (48 mg, 0.061 mmol) and PPh_3 (34 mg, 0.128 mmol) in toluene (20 mL) was refluxed for 2 h, forming a deep red solution. The solvent was removed and the residue dissolved in CH_2Cl_2 and chromatographed on TLC plates (Al_2O_3, 30:70 CH_2Cl_2/cyclohexane). **5** was isolated from a major red band located approximately half-way up the plate (20.5 mg, 32.0%). Alternatively, a refluxing, toluene solution of **4** produced **5** in approximately the same yield: IR (c-hex, 298 K) ν_{CO} (cm^{-1}) 2032 m, 2007 vs, 1982 s, 1952 s, 1939 vw; ^{1}H NMR (C_6D_6, 298 K, 200 MHz) δ (ppm) 7.8−6.2 (m); ^{31}P NMR (C_6D_6, 298 K, 200 MHz) δ (ppm) 215.0 (d, J = 6.7 Hz), 40.6 (s, br). Anal. Calcd for $C_{43}H_{29}O_7Ru_3P_2S{\cdot}0.5CH_2Cl_2$ (1099.3): C, 47.5; H, 2.75. Found: C, 47.0; H, 2.94.

Synthesis of (μ_2-H)Ru$_3$(CO)$_7$(μ_2,η^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)(μ_3,η^2-SCNHPhNPh) (6). A solution of **1** (30 mg, 0.038 mmol) and (diphenylphosphino)ethane (16 mg, 0.040 mmol) in CH_2Cl_2 was stirred for 30 min. The solvent volume was reduced to approximately 3 mL and an excess of hexanes layered on top. After 24 h, the product could be collected as an orange crystalline solid (35.3 mg, 82.5%): IR (c-hex, 298 K) ν_{CO} (cm^{-1}) 2043 s, 1997 vs, 1968 s, 1953 m, 1938 m; IR (KBr) ν_{NH} (cm^{-1}) 3340 wm, ν_{NCN} (cm^{-1}) 1573 m; ^{1}H NMR ($CDCl_3$, 298 K, 200 MHz) δ (ppm) 7.56−6.85 (m, 30H), 6.06 (s, 1H), 2.00 (d, J = 12.5 Hz, 4H), −12.94 (t, J = 13.0 Hz, 1H); ^{31}P NMR ($CDCl_3$, 298 K, 200 MHz) δ (ppm) 18.53 (s). Anal. Calcd for $C_{46}H_{36}N_2O_7Ru_3P_2S{\cdot}0.5CH_2Cl_2$ (1168.5): C, 47.7; H, 3.19; N, 2.39. Found: C, 47.7; H, 3.40; N, 1.91.

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Supporting Information Available: Tables of positional and thermal parameters and complete tables of bond lengths and angles and least-squares planes for **3**, **5**, and **6** (27 pages). Ordering information available on any current masthead page.

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