Organometallics **2003,** *22,* 1065−1071

Preparation of a Heterobimetallic Cluster with Bridging Sulfido and Thiolato Ligands [{(η^5-C$_5$Me$_5$)Ru}{(η^5-C$_5$Me$_5$)Ir}$_2$(μ_3-S)(μ_2-SCH$_2$CH$_2$CN)$_2$Cl] and Its Transformations into Alkyne, CO, Isocyanide, and Iminoacyl Clusters

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Received September 30, 2002

A diiridium complex containing bridging sulfido and thiolato ligands [Cp*Ir(μ-S)(μ-SCH$_2$CH$_2$CN)$_2$IrCp*] (Cp* = η^5-C$_5$Me$_5$) reacted with [(Cp*Ru)$_4$(μ_3-Cl)$_4$] in THF at room temperature to afford the trinuclear sulfido-thiolato cluster [(Cp*Ru)(Cp*Ir)$_2$(μ_3-S)(μ_2-SCH$_2$CH$_2$CN)$_2$Cl] (**4**). Treatment of **4** with HC≡CCOOMe, CO, and 2,6-Me$_2$C$_6$H$_3$NC (XyNC) at room temperature in the presence of KPF$_6$ resulted in the incorporation of these molecules into the Ir$_2$ or Ir site of this cluster core, yielding [(Cp*Ru)(Cp*Ir)$_2$(μ_3-S)(μ_2-SCH$_2$CH$_2$CN)$_2$(μ_2-HC═CCOOMe)][PF$_6$] (**5**) and [(Cp*Ru)(Cp*Ir)$_2$(μ_3-S)(μ_2-SCH$_2$CH$_2$CN)$_2$(L)][PF$_6$] (L = CO (**7**), XyNC). On the other hand, **4** reacted with excess KPF$_6$ along with 1 equiv of 2,6-dimethylpyridinium chloride to give [(Cp*Ru)(Cp*Ir)$_2$(μ_3-S)(μ_2-SCH$_2$CH$_2$CN)(μ_3-SCH$_2$CH$_2$C═NH)][PF$_6$]$_2$ (**9′**), which presumably formed through the binding of the CN group in one cyanoethylthiolato ligand to the Ir$_2$ site, followed by the protonation of its N atom. Single-crystal X-ray analyses were undertaken to determine the detailed structures for **4**, **5**, **7**, and **9′**.

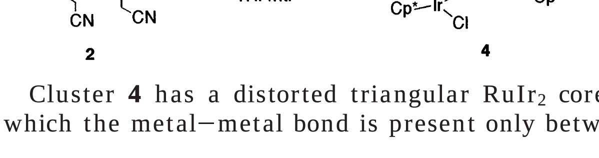
Introduction

Our continuing pursuit of the versatile precursors to prepare the multimetallic cores with bridging sulfur coligands has revealed recently that the dinuclear complexes such as [Cp*MCl(μ-SH)$_2$MCp*Cl] (M = Ru, Rh, Ir; Cp* = η^5-C$_5$Me$_5$), [Cp$_2$Ti(μ-SH)$_2$RuCp*Cl] (Cp = η^5-C$_5$H$_5$), and [M(═S)(L)(μ-S)$_2$M(═S)(L)] (M = Mo, W: L = dithiocarbamate) can incorporate a variety of one or two metal (M′) species into their metal-sulfur sites, yielding the clusters consisting of trinuclear M′M$_2$(μ_3-S)$_2$ and M′M$_2$(μ_3-S)(μ_2-S)$_3$ cores along with the cubane-type M′$_2$M$_2$(μ_3-S)$_4$ chromophores.[1] These studies have been extended more recently to the attempt to use diiridium complexes containing three or more hydrosulfido ligands [Cp*Ir(μ-SH)$_3$IrCp*]Cl (**1**) and [Cp*Ir(SH)(μ-SH)$_2$IrCp*(SH)] for derivatizing homo- and heterometallic clusters, which has turned out to be successful for the latter, leading to the isolation of certain Ir$_3$ and Pd$_2$Ir$_2$ sulfido-hydrosulfido clusters.[2] For the former complex **1**, although transformations into the metal-sulfur clusters are still elusive, the reaction with 2 equiv of CH$_2$═CHCN in the presence of excess NEt$_3$ has been demonstrated to afford the sulfido-thiolato complex [Cp*Ir(μ-S)(μ-SCH$_2$CH$_2$CN)$_2$IrCp*] (**2**).[3]

Now we have found that **2**, when treated with the Ru(II) complex [(Cp*Ru)$_4$(μ_3-Cl)$_4$] (**3**), gives a new RuIr$_2$ trinuclear sulfido-thiolato cluster. In this paper, we wish to describe the characterization of this bimetallic cluster along with its reactivities toward small molecules such as alkyne, CO, and isocyanide. Preparation of the RuIr$_2$ cluster from **2** has been reported briefly as part of the previous communication.[3a]

Results and Discussion

Synthesis and Characterization of the RuIr$_2$ Cluster. Treatment of **2** with 0.25 equiv of the tetranuclear Ru complex **3** in THF at room temperature resulted in the incorporation of a Cp*RuCl fragment into the diiridium core in **2**, yielding the RuIr$_2$ cluster [(Cp*Ru)(Cp*Ir)$_2$Cl(μ_3-S)(μ_2-SCH$_2$CH$_2$CN)$_2$] (**4**) (eq 1). Cluster **4** was isolated as dark green crystals in 69% yield and whose structure has been determined by single-crystal X-ray analysis. An ORTEP drawing is depicted in Figure 1, while the important bonding parameters are listed in Table 1.



(1)

Cluster **4** has a distorted triangular RuIr$_2$ core in which the metal−metal bond is present only between

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10.1021/om0208117 CCC: $25.00
Publication on Web 01/28/2003

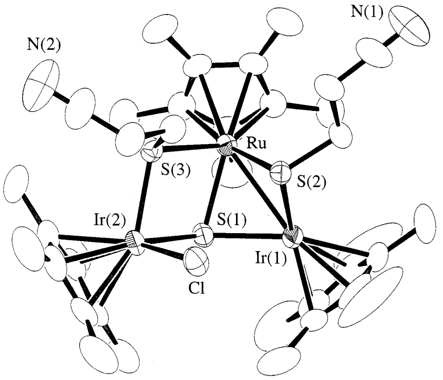

Figure 1. Molecular structure of **4**. Hydrogen atoms as well as solvating benzene and hexane molecules are omitted for clarity.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) in 4

(a) Distances			
Ir(1)−Ru	2.8362(5)	Ir(1)···Ir(2)	4.1529(3)
Ir(2)···Ru	3.6922(6)		
Ir(1)−S(1)	2.289(1)	Ir(1)−S(2)	2.273(1)
Ir(2)−S(1)	2.369(1)	Ir(2)−S(3)	2.383(1)
Ir(1)···Cl	3.981(2)	Ir(2)−Cl	2.404(1)
Ru−S(1)	2.362(1)	Ru−S(2)	2.364(1)
Ru−S(3)	2.424(2)		
(b) Angles			
S(1)−Ir(1)−S(2)	89.04(5)	S(1)−Ir(2)−S(3)	78.63(5)
S(1)−Ir(2)−Cl	95.21(5)	S(3)−Ir(2)−Cl	93.20(5)
S(1)−Ru−S(2)	85.19(5)	S(1)−Ru−S(3)	77.97(5)
S(2)−Ru−S(3)	86.93(5)		
Ir(1)−S(1)−Ir(2)	126.13(6)	Ir(1)−S(1)−Ru	75.13(4)
Ir(2)−S(1)−Ru	102.57(5)	Ir(1)−S(2)−Ru	75.38(4)
Ir(2)−S(3)−Ru	100.35(5)		

the Ru atom and one Ir atom. Thus, the Ru−Ir(1) distance at 2.8362(5) Å is much shorter than those between Ru and Ir(2) of 3.6922(6) Å and between two Ir atoms of 4.1529(3) Å. Three metal centers are connected by a μ_3-S ligand, and the two Ru−Ir edges are each bridged further by one thiolato ligand originally bound to two Ir atoms in **2**. Mutual orientation of the two cyanoethyl groups in these thiolato ligands is anti. The Cl ligand coordinates to only Ir(2) as a terminal ligand; separations from Ir(2) and Ir(1) are 2.404(1) and 3.981(2) Å, respectively. Thus, if the Ru−Ir(1) bond is ignored, the Ru and Ir(2) atoms have a three-legged piano stool structure, while the geometry around Ir(1) is a two-legged piano stool. The oxidation states of metals are assignable formally to be Ru(II)Ir(III)$_2$. By assuming the Ru−Ir bond as a dative one from Ru to Ir(1), the EAN rule is satisfied for all three metal centers.

Due to these distorted features of the RuIr$_2$ triangle, coordination of the μ_3-S is quite unsymmetrical; the M−S(1) distance for Ir(1) with the two-legged piano stool structure at 2.289(1) Å is significantly shorter than the other Ru−S(1) and Ir(2)−S(1) bond lengths at 2.362(1) and 2.369(1) Å, respectively, and the M−S(1)−M′ angles vary from 75.13(4)° for M, M′ = Ru and Ir(1) to 126.13(6)° for M, M′ = Ir(1) and Ir(2). The Ir(III)−S and Ru(II)−S bond distances for the essentially symmetrical μ_3-S ligands are, for example, 2.289(3) Å in [(Cp*Ir)$_3$(μ_3-S)$_2$][BF$_4$]$_2$,[4] 2.367(3)−2.380(3) Å in [(Cp*Ir)$_4$(μ_3-S)$_4$],[5] 2.263(2)−2.272(1) Å in [{(η^6-*p*-cymene)Ru}$_3$(μ_3-S)$_2$][PF$_6$]$_2$,[6] and 2.380(1)−2.412(2) Å in [{(η^6-*p*-cymene)Ru}$_4$(μ_3-S)$_4$].[7] As for the thiolato ligands, the M−S bond relating to Ir(1) (2.273(1) Å) is shorter than the other three bonds (2.364(1)−2.424(2) Å), and the thiolato ligand bridging the Ru−Ir(1) bond has a more acute M−S−M′ angle of 75.38(4)° than that bound to two metals without a direct M−M′ bonding interaction, Ru and Ir(2) (100.35(5) Å). For comparison, the Ir(III)−S bond lengths in [Cp*IrCl(μ-SPr^i)$_2$IrCp*Cl] are 2.391(2) and 2.400(2) Å,[8] and those associated with the μ-thiolato ligands in **2** are in the range 2.382(2)−2.395(2) Å,[3] while the Ru(II)−S bond distances in [{Cp*Ru(CO)}$_2$(μ-SBu^t)$_2$] are 2.419(2) and 2.424(2) Å.[9]

In accordance with this X-ray structure, the ^{1}H NMR spectrum of **4** dissolved in C$_6$D$_6$ shows three singlets assignable to the Cp* groups at δ 1.44, 1.51, and 1.83 with the same intensity, indicating that the inequivalence of two Ir atoms is maintained even in solution at room temperature. The IR spectrum exhibited the ν(C≡N) band at 2245 cm^{-1}, which is in the region for the free aliphatic nitriles (2260−2240 cm^{-1}).

Reactions of 4 with HC≡CCOOMe. Reactivities of the new cluster **4** toward a range of small molecules have been investigated. Reaction with 4 equiv of the alkyne HC≡CCOOMe in THF at room temperature resulted in the almost quantitative recovery of **4**. However, the concomitant formation of a small amount of the alkyne trimers C$_6$H$_3$(COOMe)$_3$ was observed. Thus, the reaction of **4** with 200 equiv of HC≡CCOOMe in THF was carried out at 50 °C for 2 days, which turned out to afford a mixture of the isomers 1,2,4- and 1,3,5-C$_6$H$_3$(COOMe)$_3$ in a ratio of 56:44. The combined yield of these trimers was 52%, which corresponds to 34 mol per mol **4** initially charged.

Although it is well known that cyclotrimerization of alkynes is catalyzed by various transition metal complexes, the reactions promoted by well-defined cluster catalysts are relatively limited.[10] Previously we observed facile conversion of HC≡CCOOMe into these trimers in the presence of the Ru(II) sulfido cluster [(Cp*Ru)$_3$(μ_3-S)(μ_3-Cl)]. However, this transformation was concluded to be catalyzed by a small amount of the unknown Ru species generated in situ rather than the parent cluster.[11] In the reaction reported here, the ^{1}H NMR study of the reaction mixture showed that **4** decomposed gradually under these conditions and the rate of the formation of the trimers increased as the degradation of **4** proceeded. Hence, this trimerization reaction is also presumed to be catalyzed by the uncharacterizable species generated in situ through degradation.

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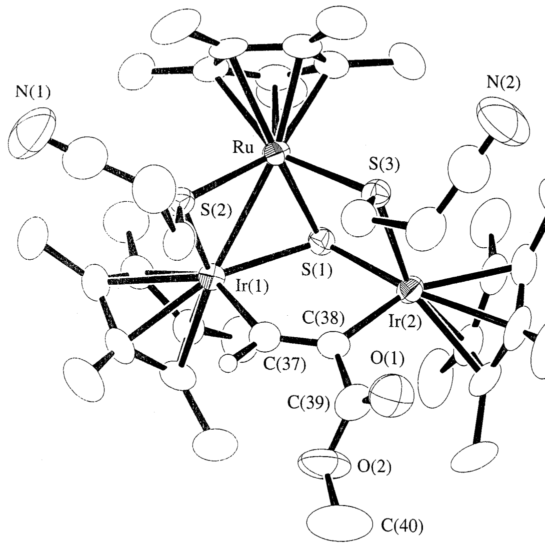
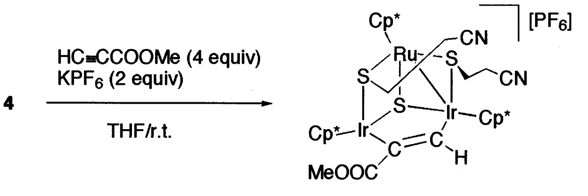


Figure 2. Molecular structure of **5**. Hydrogen atoms are omitted for clarity except for that bound to C(37).

It has been found that if the reaction of **4** with 4 equiv of HC≡CCOOMe is carried out in the presence of 2 equiv of KPF_6, incorporation of the alkyne into the $RuIr_2$ core takes place to give the well-defined cluster $[(Cp^*Ru)(Cp^*Ir)_2(\mu_3\text{-}S)(\mu_2\text{-}SCH_2CH_2CN)_2(\mu_2\text{-}HC{=}CCOOMe)][PF_6]$ (**5**), which was isolated as black crystals in moderate yield (eq 2). Replacement of the coordinated Cl by a noncoordinating PF_6 anion might generate the vacant site and facilitate the binding of the alkyne. Even in the presence of an excess of the alkyne, **5** did not react further, and for all the reactions carried out in the presence of KPF_6 formation of the alkyne trimers was not observed.



5 (2)

The structure of **5** has been determined unambiguously by the X-ray analysis. An ORTEP drawing of the cation is depicted in Figure 2, while the important interatomic distances and angles are listed in Table 2. As shown in Figure 2, **5** has a $RuIr_2S_3$ core analogous to that in **4**. Thus, in the $RuIr_2$ triangular core the metal−metal bonding is present only between Ru and Ir(1). The three metal centers are connected by one μ_3-S ligand, and two μ_2-thiolato ligands each bridge the Ru−Ir edges. With respect to the metal−metal separations, the Ir(1)−Ru and Ir(2)···Ru distances are shorter only slightly, whereas the Ir(1)···Ir(2) distance is significantly shortened by ca. 0.3 Å, as compared to those in **4**. Accordingly, the Ir(1)−S(1)−Ir(2) angle becomes smaller and the S(1)−Ru−S(2) and S(1)−Ru−S(3) angles become larger than those in **4**. As for the two thiolato ligands, the cyanoethyl groups are mutually syn, in contrast to their anti configuration in the parent cluster **4**, and the four-membered $IrRuS_2$ rings are puckered only slightly with the dihedral angles of 164.6° and 171.5° around the Ir−Ru vectors of the Ir(1)−S(1)−Ru−S(2) and Ir(2)−S(1)−Ru−S(3) rings, respectively.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) in 5

(a) Distances

Ir(1)−Ru	2.7859(5)	Ir(1)···Ir(2)	3.8463(3)
Ir(2)···Ru	3.6551(5)		
Ir(1)−S(1)	2.306(1)	Ir(1)−S(2)	2.285(2)
Ir(1)−C(37)	2.042(6)	Ir(2)−S(1)	2.309(1)
Ir(2)−S(3)	2.362(2)	Ir(2)−C(38)	2.054(6)
Ru−S(1)	2.318(2)	Ru−S(2)	2.300(1)
Ru−S(3)	2.412(1)	C(37)−C(38)	1.331(8)

(b) Angles

S(1)−Ir(1)−S(2)	104.62(5)	S(1)−Ir(1)−C(37)	85.4(2)
S(2)−Ir(1)−C(37)	89.7(2)	S(1)−Ir(2)−S(3)	78.17(5)
S(1)−Ir(2)−C(38)	85.7(2)	S(3)−Ir(2)−C(38)	87.4(2)
S(1)−Ru−S(2)	103.78(5)	S(1)−Ru−S(3)	77.01(5)
S(2)−Ru−S(3)	105.70(5)		
Ir(1)−S(1)−Ir(2)	112.89(6)	Ir(1)−S(1)−Ru	74.10(4)
Ir(2)−S(1)−Ru	104.37(5)	Ir(1)−S(2)−Ru	74.81(4)
Ir(2)−S(3)−Ru	99.93(5)		
Ir(1)−C(37)−C(38)	128.8(4)	Ir(2)−C(38)−C(37)	126.8(4)
Ir(2)−C(38)−C(39)	118.8(4)	C(37)−C(38)−C(39)	114.4(5)

The five-membered ring defined by the two Ir and the μ_3-S atoms as well as the two C atoms of the coordinated alkyne are strictly planar. The C(39)−O(1) double bond in the COOMe moiety is not coincident with this plane presumably because of the steric repulsion between the carbonyl O(1) atom and the Cp* ligand bonded to Ir(2). The C(37)−C(38) distance at 1.331(8) Å is in good agreement with the C=C double bond length in the unconjugated C=C−C=O compounds (av 1.331 Å).[12] The sum of the three observed interatomic angles around the C(38) atom is 360.0°, indicating clearly the sp^2-hybridized nature of this C atom in this five-membered ring. The ^{13}C NMR data are also consistent with this feature, exhibiting signals at δ 159.9 and 157.0 for C(37) and C(38), respectively, with $^1J_{C-H} = 150$ Hz for the former. For common organic compounds, the alkynic carbons are known to resonate in the range, e.g., 60−90 ppm, while the alkenic carbons appear from 100 to 150 ppm. The $^1J_{C-H}$ values are 249.0 and 156.4 Hz for acetylene and ethylene, respectively.[13]

In this reaction, the alkyne is presumed to bind to the Ir(III)/Ir(III) site in the coordinatively unsaturated species $[(Cp^*Ru)(Cp^*Ir)_2(\mu_3\text{-}S)(\mu_2\text{-}SCH_2CH_2CN)_2]^+$ generated by dissociation of the Cl ligand. By formation of two Ir−C σ bonds, the formal oxidation state of the $RuIr_2$ core changes from +8 to +10. Each metal should be assigned as Ru(III), Ir(III), and Ir(IV), where the metal−metal bond is present between Ru(III) and Ir(IV). Assignment of Ir(2) without the Ru−Ir bond being Ir(III) is consistent with the fact that this lower valent Ir atom attaches to the C(38) atom bearing the strongly electron-withdrawing COOMe substituent rather than the nonsubstituted C(37) atom.

Alkynes have been shown to be incorporated into the multimetallic sites in various manners.[14] Coordination of the alkynes parallel to the metal−metal axis has already been precedented, for example, in diiridium and diruthenium complexes with bridging $Ph_2PCH_2PPh_2$

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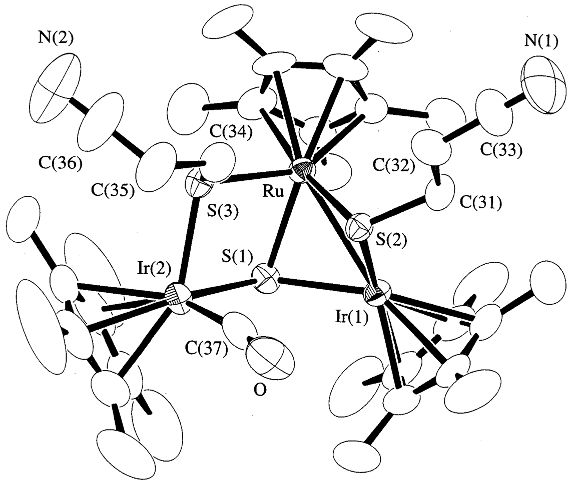


Figure 3. Molecular structure of **7**. Hydrogen atoms and solvating acetonitrile molecule are omitted for clarity.

(dppm) ligands such as $[Ir_2(CO)_2(\mu\text{-}HC{=}CH)(\mu\text{-}CCHPh)(\mu\text{-}dppm)_2]$ (**6**)[15] and $[Ru_2(CO)_4(\mu\text{-}PhC{=}CCOMe)(\mu\text{-}dppm)_2]$[16] as well as in the Ir_4 cluster, $[Ir_4(CO)_8(\mu_2\text{-}MeOCOC{=}CCOOMe)_2(\mu_4\text{-}MeOCOCCCOOMe)_2]$.[17] The C=C bond distances in these μ_2-alkyne moieties are 1.316(9), 1.343(6), and 1.278(11) Å, respectively. The NMR chemical shifts of the μ-HC=CH protons in **6**[15] and other diiridium complexes relating to **6**[18] are in the range 8−11 ppm, which are comparable to that for **5** of 8.11 ppm.

Reactions of 4 with CO and Isocyanide. In the presence of KPF_6, **4** dissolved in MeCN also reacts with CO (1 atm) at room temperature to afford a cationic monocarbonyl cluster $[(Cp^*Ru)(Cp^*Ir)_2(\mu_3\text{-}S)(\mu_2\text{-}SCH_2CH_2CN)_2(CO)][PF_6]$ (**7**) (eq 3), whose structure has been determined by X-ray analysis. As shown in Figure 3, the structure of the cation in **7** is quite analogous to that of **4** except that the Cl ligand in **4** is replaced by the terminal CO ligand. The interatomic distances and angles observed for the $RuIr_2S_3$ core of **7** listed in Table 3 are essentially the same as those of **4** summarized in Table 1. The Ir−C−O angle is almost linear (170(1)°), and the C−O bond length at 1.12(1) Å is typical of the terminal CO ligand. In the IR spectrum, an intense $\nu(C{\equiv}O)$ band appears at 2020 cm^{-1}, which is considerably lower than those of the Ir(III) complexes of the type $[IrX_3(CO)(L)_2]$ (X = Cl, Br; L = tertiary phosphines) in the region 2055−2085 cm^{-1},[19] presumably because of the strong electron-donating ability of the sulfur ligands. Thus, the $\nu(C{\equiv}O)$ values of 1994 cm^{-1} for $[Cp^*Ir(SPh)_2(CO)]$ and 2004 and 2011 cm^{-1} for the Ir−CO moieties in $[Cp^*Ir(CO)(\mu\text{-}SPh)_2M(CO)_4]$ with M = Cr and M = Mo, respectively, are also significantly lower.[20]

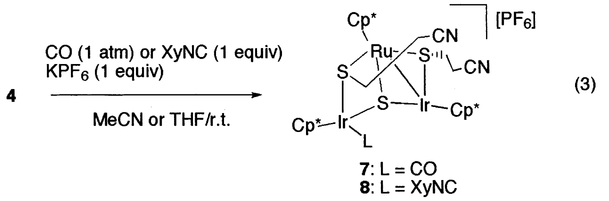
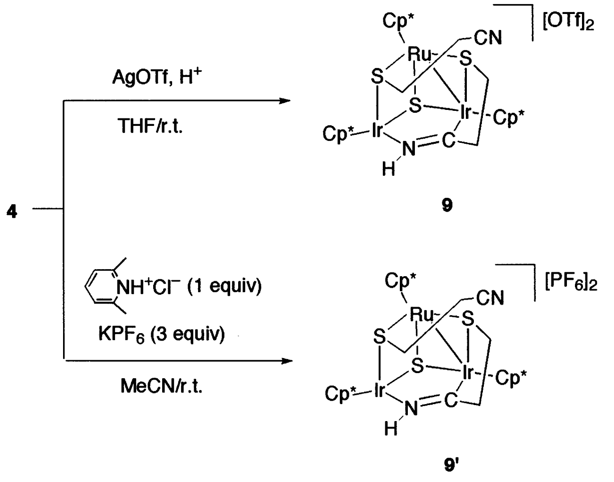


Table 3. Selected Interatomic Distances (Å) and Angles (deg) in 7

	(a) Distances		
Ir(1)−Ru	2.8394(8)	Ir(1)···Ir(2)	4.0711(6)
Ir(2)···Ru	3.6820(9)		
Ir(1)−S(1)	2.285(3)	Ir(1)−S(2)	2.275(2)
Ir(2)−S(1)	2.387(3)	Ir(2)−S(3)	2.372(3)
Ir(2)−C(37)	1.88(1)	Ru−S(1)	2.367(3)
Ru−S(2)	2.366(3)	Ru−S(3)	2.408(3)
O−C(37)	1.12(1)		
	(b) Angles		
S(1)−Ir(1)−S(2)	88.54(9)	S(1)−Ir(2)−S(3)	77.87(9)
S(1)−Ir(2)−C(37)	94.2(4)	S(3)−Ir(2)−C(37)	97.0(4)
S(1)−Ru−S(2)	84.51(9)	S(1)−Ru−S(3)	77.55(9)
S(2)−Ru−S(3)	87.50(9)		
Ir(1)−S(1)−Ir(2)	121.2(1)	Ir(1)−S(1)−Ru	75.21(8)
Ir(2)−S(1)−Ru	101.50(10)	Ir(1)−S(2)−Ru	75.41(7)
Ir(2)−S(3)−Ru	100.78(10)		
Ir(2)−C(37)−O	170(1)		

Scheme 1



Treatment of **4** with 1 equiv of XyNC (Xy = 2,6-$Me_2C_6H_3$) in THF at room temperature also resulted in the formation of the isocyanide adduct $[(Cp^*Ru)(Cp^*Ir)_2(\mu_3\text{-}S)(\mu_2\text{-}SCH_2CH_2CN)_2(CNXy)][PF_6]$ (**8**) in high yield (eq 3). The IR spectrum exhibits a strong $\nu(N{\equiv}C)$ band at 2114 cm^{-1} assignable to the isocyanide N≡C bond in addition to the weak $\nu(C{\equiv}N)$ band due to the cyanoethyl C≡N bonds (2249 cm^{-1}). The former value is consistent with the terminal end-on coordination of XyNC to one Ir center as clarified for the CO ligand in **7**.

Formation of the μ-Iminoacyl Cluster from 4. Finally, attempts were made to isolate the coordinatively unsaturated intermediate(s) generated by the removal of the Cl ligand by treatment of **4** with KPF_6. However, the ^1H NMR spectra have disclosed that without any substrate molecules reactions of **4** with KPF_6 do not occur. In contrast, from the reaction mixture obtained from **4** and 1 equiv of AgOTf (OTf = OSO_2CF_3) in THF at room temperature was isolated the μ-iminoacyl cluster $[(Cp^*Ru)(Cp^*Ir)_2(\mu_3\text{-}S)(\mu_2\text{-}SCH_2CH_2CN)(\mu_3\text{-}SCH_2CH_2C{=}NH)][OTf]_2$ (**9**) in 26% yield (Scheme

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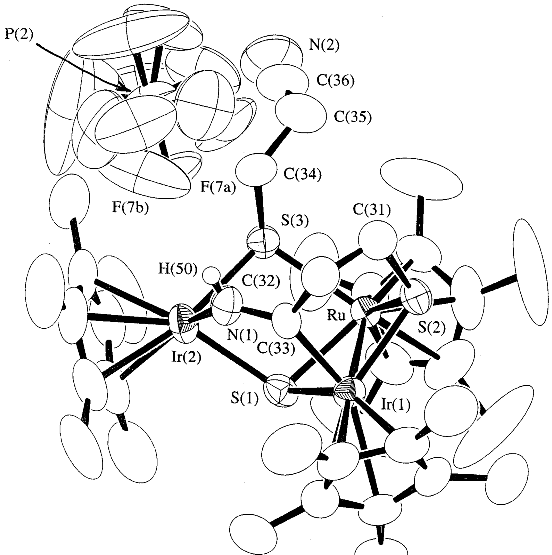

Figure 4. Molecular structure of **9′**. Hydrogen atoms except for that on N(1) and solvating acetone molecule are omitted for clarity. Among two PF_6 anions, only one disordered anion having a hydrogen-bonding interaction between the NH protons is shown.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) in 9′

(a) Distances			
Ir(1)−Ru	2.7746(6)	Ir(1)···Ir(2)	3.7860(4)
Ir(2)···Ru	3.6691(5)		
Ir(1)−S(1)	2.301(2)	Ir(1)−S(2)	2.308(2)
Ir(1)−C(33)	2.017(6)	Ir(2)−S(1)	2.331(2)
Ir(2)−S(3)	2.389(2)	Ir(2)−N(1)	2.055(6)
Ru−S(1)	2.322(2)	Ru−S(2)	2.322(2)
Ru−S(3)	2.426(2)	N(1)−C(33)	1.263(8)
N(1)−H(50)	0.73(6)	F(7a)···H(50)	2.41(6)
F(7b)···H(50)	2.71(8)		
(b) Angles			
S(1)−Ir(1)−S(2)	105.33(6)	S(1)−Ir(1)−C(33)	87.3(2)
S(2)−Ir(1)−C(33)	79.6(2)	S(1)−Ir(2)−S(3)	77.72(6)
S(1)−Ir(2)−N(1)	85.5(2)	S(3)−Ir(2)−N(1)	85.1(2)
S(1)−Ru−S(2)	104.22(6)	S(1)−Ru−S(3)	77.16(6)
S(2)−Ru−S(3)	106.06(6)		
Ir(1)−S(1)−Ir(2)	109.63(7)	Ir(1)−S(1)−Ru	73.76(5)
Ir(2)−S(1)−Ru	104.10(7)	Ir(1)−S(2)−Ru	73.63(5)
Ir(2)−S(3)−Ru	99.29(6)	Ir(2)−N(1)−C(33)	128.5(5)
Ir(1)−C(33)−N(1)	126.4(5)	Ir(1)−C(33)−C(32)	113.1(4)
N(1)−C(33)−C(32)	119.9(6)		

1). This product is presumed to be formed through the coordination of the CN group in one cyanoethylthiolato ligand to the Ir_2 site, followed by the protonation of the coordinated N atom. The proton source of the iminoacyl ligand may be adventitious moisture. As expected, when the reactions of **4** with KPF_6 (3 equiv) were carried out in the presence of a stoichiometric amount of the proton donors, the μ-iminoacyl cluster $[(Cp^*Ru)(Cp^*Ir)_2(\mu_3\text{-}S)(\mu_2\text{-}SCH_2CH_2CN)(\mu_3\text{-}SCH_2CH_2C{=}NH)][PF_6]_2$ (**9′**) was obtained in higher yields, which has been fully characterized by X-ray analysis (vide infra). When HCl was used as the proton source, the reaction was not clean due to the formation of a significant amount of the uncharacterized byproduct in addition to **9′**. In contrast, the reaction of **4** with 2,6-dimethylpyridinium chloride gave the mixture containing **9′** as the sole product detectable by ^1H NMR spectroscopy, which was isolated as brown crystals in 65% yield (Scheme 1).

The structure of **9′** has been fully characterized by X-ray analysis by using a single crystal of composition **9′**·Me_2CO grown from acetone−hexane. As shown in Figure 4, the vacant site generated by the dissociation of the Cl ligand is occupied by the μ-iminoacyl moiety derived from the terminal CN group of one cyanoethylthiolato ligand in **4**. Coordination of the −C≡N moiety to the Ir_2 site and the following Ru−Ir bond formation probably proceed analogously to the formation of the alkyne cluster **5**, and the resultant Ir−C=N−Ir moiety undergoes facile protonation at the sp^2 N atom, yielding **9′**. Although the reaction was carried out in MeCN as solvent, only the CN group in the thiolato ligand was incorporated into the cluster site.

Figure 4 and Table 4 show that the $RuIr_2S_3$ core structure in **9′** is in good agreement with that in the alkyne adduct **5** except for the considerably shorter Ir(1)···Ir(2) separation of 3.7860(4) Å than that in **5** (3.8463(3) Å). The C−N bond distance at 1.263(8) Å is only slightly shorter than the C−N double bond distances of ca. 1.28 Å in imines and oximes,[12] indicating the double bond nature of this linkage in **9′**. The sum of the three interatomic angles around the C(33) atom is 359.4°, which supports the sp^2 character of this C atom. The iminoacyl hydrogen in **9′** is found from the Fourier map; the distances at 2.41(6) and 2.71(8) Å of this proton from F(7a) and F(7b), which are one F atom disordered around the P atom in one of the two PF_6 anions, suggest the presence of hydrogen-bonding interactions.

It is to be noted that the examples of well-defined bridging iminoacyl ligands are still quite limited; the μ_2-iminoacyl moieties parallel to the metal−metal bond were observed previously, for example, in fully characterized $[HOs_3(CO)_9(PMe_2Ph)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C{=}NH)]$ (**10**) obtained from $[H_2Os_3(CO)_9(PMe_2Ph)]$ with CF_3CN[21] and $[\{Fe(\eta^2\text{-}ArC{=}NBu^t)\}_2(\mu\text{-}ArC{=}NBu^t)_2]$ (**11**, Ar = 2,4,6-$Me_3C_6H_2$) from $[(FeAr)_2(\mu\text{-}Ar)_2]$ with Bu^tNC.[22] The C=N bond distances at 1.31(1) Å in **10** and 1.292(6) Å in **11** are somewhat longer than that in **9′** (1.263(8) Å). In the ^1H NMR spectrum of **9′** dissolved in CD_3CN, the iminoacyl proton resonates at δ 9.71 as a broad singlet, while that in **10** is reported to appear at δ 8.73 ($CDCl_3$ solution).[21] The ^{13}C NMR spectrum was also recorded for **9′**, which showed the iminoacyl C resonance at δ 226.0. This value is comparable to those of the spectroscopically characterized μ_2-iminoacyl complexes $[\{Fe(CO)_3\}_2(\mu\text{-}RC{=}NPh)(\mu\text{-}SMe)]$ prepared from $[Fe_3(CO)_{12}]$ and RC(SR)=NPh (R = Me, Et, Ph) in the range δ 230−237.[23]

In contrast, the iminoacyl ligand in $[\{(\eta^5\text{-}C_5H_4Pr^i)WCl_2\}_2(\mu\text{-}Cl)(\mu\text{-}EtC{=}NH)]$ bridging the two W atoms perpendicularly to the W−W bond has a much longer C=N bond with the C−N distance at 1.405(8) Å,[24] which is rather close to the typical C−N single bond distance of 1.47 Å. Consistently, the NH proton in this W complex is observed in much higher field (δ 5.89) in its ^1H NMR spectrum (CD_2Cl_2 solution) as compared to **9′** and **10**.

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Table 5. Crystal Data for $\mathbf{4}\cdot 1/2C_6H_6\cdot 1/2C_6H_{14}$, $\mathbf{5}\cdot$MeCN, 7, and $\mathbf{9'}\cdot Me_2CO$

	$\mathbf{4}\cdot 1/2C_6H_6\cdot 1/2C_6H_{14}$	$\mathbf{5}\cdot$MeCN	**7**	$\mathbf{9'}\cdot Me_2CO$
formula	$C_{42}H_{63}N_2S_3ClRuIr_2$	$C_{42}H_{60}N_3O_2F_6PS_3RuIr_2$	$C_{37}H_{53}N_2OF_6PS_3RuIr_2$	$C_{39}H_{60}N_2OF_{12}P_2S_3RuIr_2$
fw	1213.12	1365.61	1268.49	1444.53
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	12.531(1)	14.664(3)	9.059(1)	20.821(2)
b, Å	14.223(1)	18.784(3)	11.981(3)	12.079(4)
c, Å	15.012(1)	17.849(2)	20.135(2)	21.755(2)
α, deg	75.305(7)	90	89.81(1)	90
β, deg	68.366(7)	99.15(1)	87.187(9)	115.388(6)
γ, deg	66.391(7)	90	84.24(1)	90
V, Å^3	2261.3(4)	4853(1)	2171.5(6)	4929(1)
Z	2	4	2	4
ρ_{calcd}, g cm^{-3}	1.782	1.869	1.940	1.941
μ, cm^{-1}	64.44	60.15	67.12	59.58
cryst size, mm^3	0.5 × 0.4 × 0.2	0.6 × 0.5 × 0.3	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.4
no. of unique reflns	7945	11 126	9975	11 355
no. of data used	6690 ($I > 3\sigma(I)$)	8524 ($I > 3\sigma(I)$)	5846 ($I > 3\sigma(I)$)	7869 ($I > 3\sigma(I)$)
no. of variables	454	542	479	618
transmn factor	0.3844−0.9997	0.4262−0.9994	0.7076−0.9992	0.8061−0.9996
R^a	0.026	0.032	0.043	0.034
$R_w{}^b$	0.029	0.035	0.041	0.036
GOF^c	1.91	1.56	1.48	1.19

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$ ($w = [\{\sigma(F_o)\}^2 + (p^2/4)F_o{}^2]^{-1}$). [c] GOF $= [\sum w(|F_o| - |F_c|)^2/\{$(no. observed) − (no. variables)$\}]^{1/2}$.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified by common procedures. Complexes **2**[3] and **3**[25] were prepared according to literature methods, while other reagents were obtained commercially and used as received. The ^{1}H NMR spectra were recorded on a JEOL alpha-400 spectrometer, and the IR spectra were obtained from a JASCO FT/IR-420 spectrometer. The GLC and GC−MS studies were carried out by using a Shimadzu GC-14B chromatograph equipped with a CBP10 capillary column and a Shimadzu GCMS-QP5050 spectrometer. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of 4. A THF solution (30 mL) containing **2** (200 mg, 0.233 mmol) and **3** (63 mg, 0.058 mmol) was stirred at room temperature for 24 h. The resultant dark green solution was dried in vacuo, and the residue was extracted with benzene. Addition of hexane to the concentrated extract gave $\mathbf{4}\cdot 1/2C_6H_6\cdot 1/2C_6H_{14}$ as dark green needles (196 mg, 69% yield). IR (KBr): ν(C≡N), 2245 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.44, 1.51, and 1.83 (s, 15H each, Cp*), 0.96 (dt, J = 12 and 8 Hz, 1H, CH_2), 1.73 (ddd, J = 17, 12, and 5 Hz, 1H, CH_2), 1.9−2.1 (m, 3H, CH_2), 2.37 (td, J = 12 and 5 Hz, 1H, CH_2), 2.78 (td, J = 12 and 5 Hz, 1H, CH_2), 3.27 (dt, J = 12 and 6 Hz, 1H, CH_2). Anal. Calcd for $C_{42}H_{63}N_2S_3ClIr_2Ru$: C, 41.58; H, 5.23; N, 2.31. Found: C, 41.76; H, 5.28; N, 2.30.

Preparation of 5. Into a THF solution (10 mL) of $\mathbf{4}\cdot 1/2C_6H_6\cdot 1/2C_6H_{14}$ (57 mg, 0.047 mmol) was added HC≡CCOOMe (18 μL, 0.20 mmol) and KPF_6 (18 mg, 0.10 mmol), and the mixture was stirred at room temperature for 24 h. The resulting black solution was dried and the residue was crystallized from MeCN-ether to give $\mathbf{5}\cdot$MeCN as black plates (39 mg, 61%). IR (KBr): ν(C≡N), 2247; ν(C=O), 1682 (s) cm^{-1}. ^{1}H NMR (CD_3CN): δ 1.63, 1.74, and 1.89 (s, 15H each, Cp*), 1.03 (ddd, J = 11, 10, and 7 Hz, 1H, CH_2), 1.55 (ddd, J = 12, 7, and 5 Hz, 1H, CH_2), 1.9−2.1 (m, 2H, CH_2), 2.39 (ddd, J = 12, 8, and 6 Hz, 1H, CH_2), 2.7−3.0 (m, 3H, CH_2), 3.52 (s, 3H, OMe), 8.11 (s, 1H, HCC). ^{13}C NMR (CD_3CN): δ 9.2, 10.1, 10.2 ($C_5\mathit{Me}_5$), 18.7, 20.2, 30.1, 32.6 (CH_2), 51.6 (OMe), 95.0, 101.2, 105.7 (C_5Me_5), 119.5, 119.9 (CN), 157.0 (CH=*C*COOMe), 159.9 ($^1J_{C-H}$ = 150 Hz, *C*H=CCOOMe), 175.7 (CH=C*C*OOMe). Anal. Calcd for $C_{42}H_{60}N_3O_2F_6PS_3RuIr_2$: C, 36.94; H, 4.43; N, 3.08. Found: C, 36.61; H, 4.24; N, 2.69.

Reactions of 4 with Excess HC≡CCOOMe. A THF solution (5 mL) containing **4** (11 mg, 0.0090 mmol) and HC≡CCOOMe (0.160 mL, 1.79 mmol) was stirred at 50 °C for 2 days. The GLC analysis as well as ^{1}H NMR spectroscopy of the reaction mixture showed the formation of the trimers 1,2,4- and 1,3,5-$C_6H_3(COOMe)_3$ in 52% combined yield in a ratio of 56:44, where the conversion of the alkyne was 59%. ^{1}H NMR (C_6D_6) 1,2,4-$C_6H_3(COOMe)_3$: δ 3.38, 3.43, 3.52 (s, 3H each, OMe), 7.36 (d, J = 7.6 Hz, 1H, C_6H), 7.90 (dd, J = 7.6, 1.6 Hz, 1H, C_6H), 8.51 (d, J = 1.6 Hz, 1H, C_6H); 1,3,5-$C_6H_3(COOMe)_3$: δ 3.41 (s, 9H, OMe), 8.99 (s, 3H, C_6H).

Preparation of 7. A MeCN solution (5 mL) of $\mathbf{4}\cdot 1/2C_6H_6\cdot 1/2C_6H_{14}$ (57 mg, 0.047 mmol) and KPF_6 (9 mg, 0.05 mmol) was stirred at room temperature for 24 h under CO (1 atm), and the resultant black-purple mixture was filtered. Addition of ether to the concentrated filtrate gave **7** as red-purple crystals (35 mg, 59% yield). IR (KBr): ν(C≡N), 2248; ν(C≡O), 2020 (s) cm^{-1}. ^{1}H NMR (CD_3CN): δ 1.71, 1.82, and 2.01 (s, 15H each, Cp*), 2.0−2.2 (m, 2H, CH_2), 2.27 (ddd, J = 13, 8, and 7 Hz, 1H, CH_2), 2.52 (ddd, J = 13, 7, and 6 Hz, 1H, CH_2), 2.65 (m, 1H, CH_2), 2.8−3.0 (m, 2H, CH_2), 3.15 (m, 1H, CH_2). Anal. Calcd for $C_{37}H_{53}N_2OF_6PS_3RuIr_2$: C, 35.03; H, 4.21; N, 2.21. Found: C, 34.93; H, 4.17; N, 2.27.

Preparation of 8. A THF solution (5 mL) of $\mathbf{4}\cdot 1/2C_6H_6\cdot 1/2C_6H_{14}$ (57 mg, 0.047 mmol), KPF_6 (9 mg, 0.05 mmol), and XyNC (7 mg, 0.05 mmol) was stirred at room temperature for 24 h. The resultant dark red solution was filtered, and hexane was added to the concentrated filtrate. Deep red crystals of $\mathbf{8}\cdot$1/2THF precipitated (56 mg, 84% yield). IR (KBr): ν(C≡N) (nitrile), 2249; ν(N≡C) (isocyanide), 2114 (s) cm^{-1}. ^{1}H NMR (CD_3CN): δ 1.72, 1.76, and 1.87 (s, 15H each, Cp*), 1.7−1.8 (m overlapping with the Cp* peaks, 1H, CH_2), 2.0−2.2 (m, 2H, CH_2), 2.6−2.8 (m, 4H, CH_2), 3.10 (ddd, J = 14, 11, and 6 Hz, 1H, CH_2), 2.61 (s, 6H, Me in Xy), 7.2−7.3 (m, 3H, C_6H_3). Anal. Calcd for $C_{47}H_{66}N_3O_{0.5}F_6PS_3RuIr_2$: C, 40.10; H, 4.73; N, 2.98. Found: C, 39.82; H, 4.67; N, 2.99.

Preparation of 9. A mixture containing $\mathbf{4}\cdot 1/2C_6H_6\cdot 1/2C_6H_{14}$ (96 mg, 0.079 mmol) and AgOTf (21 mg, 0.080 mmol) in THF (10 mL) was stirred at room temperature for 24 h, and the resultant mixture was filtered. The filtrate was dried in vacuo, and the residue was crystallized from MeCN-ether. The title compound was obtained as black crystals (29 mg, 26% yield). IR (KBr): ν(C≡N), 2245; ν(S=O), 1269, 1156; ν(N−H) 3166 cm^{-1}. ^{1}H NMR (CD_3CN): δ 1.66, 1.85, 2.04 (s, 15H each, Cp*),

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1.12 (ddd, $J = 13$, 8, and 7 Hz, 1H, CH$_2$), 1.49 (ddd, $J = 13$, 7, and 6 Hz, 1H, CH$_2$), 1.90 (overlapping with CHD$_2$CN, 1H, CH$_2$), 2.04 (overlapping with Cp*, 1H, CH$_2$), 2.21 (ddd, $J =$ 17, 7, and 6 Hz, 1H, CH$_2$), 3.42 (br q, $J = 11$ Hz, 1H, CH$_2$), 3.71 (dd, $J = 13$ and 7 Hz, 1H, CH$_2$), 3.92 (dd, $J = 14$ and 10 Hz, 1H, CH$_2$), 10.1 (br, 1H, NH). Overlapping signals were confirmed by the 2D ^{1}H$-$^{1}H NMR spectrum. Anal. Calcd for $C_{38}H_{54}N_2O_6F_6S_5RuIr_2$: C, 32.73; H, 3.90; N, 2.01. Found: C, 32.81; H, 3.92; N, 2.31.

Preparation of 9′. A mixture of **4**·1/2C$_6$H$_6$·1/2C$_6$H$_{14}$ (61 mg, 0.051 mmol), KPF$_6$ (27 mg, 0.15 mmol), and 2,6-dimethylpyridinium chloride (7.5 mg, 0.050 mmol) in MeCN (5 mL) was stirred at room temperature for 14 h. The resultant mixture was filtered, and ether was added to the concentrated filtrate to give **9′**·MeCN as brown prisms (47 mg, 65% yield). IR (KBr): ν(C≡N), 2250; ν(C═N), 1560; ν(N−H) 3253 cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 1.65, 1.84, 2.05 (s, 15H each, Cp*), 1.11 (dt, $J = 13$ and 8 Hz, 1H, CH$_2$), 1.39 (ddd, $J = 13$, 8, and 6 Hz, 1H, CH$_2$), 1.85 (overlapping with the Cp* signal, 1H, CH$_2$), 1.9−2.2 (m, 2H, CH$_2$), 3.43 (dtd, $J = 13$, 10, and 1 Hz, 1H, CH$_2$), 3.54 (br dd, $J = 13$ and 7 Hz, 1H, CH$_2$), 3.93 (ddd, $J =$ 14, 10, and 1 Hz, 1H, CH$_2$), 9.71 (br, 1H, NH). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 9.7, 10.3, and 10.6 (C$_5$*Me*$_5$), 19.0, 23.3, 34.4, and 60.2 (CH$_2$), 94.4, 104.0, and 107.1 (*C*$_5$Me$_5$), 119.3 (C≡N), 226.0 (C═NH). Anal. Calcd for $C_{38}H_{57}N_3F_{12}P_2S_3RuIr_2$: C, 31.97; H, 4.02; N, 2.94. Found: C, 31.80; H, 3.99; N, 3.08.

X-ray Crystallography. The X-ray analyses of **4**·1/2C$_6$H$_6$·1/2C$_6$H$_{14}$, **5**·MeCN, **7**, and **9′**·Me$_2$CO were carried out at room temperature on a Rigaku AFC7R diffractometer equipped with a Mo Kα source. Details of crystal and data collection parameters are listed in Table 5.

Structure solution and refinements were conducted by using the TEXSAN program package.[26] The positions of nonhydrogen atoms were determined by DIRDIF PATTY[27] and were refined anisotropically. Hydrogen atoms were placed at ideal positions and included at the final stages of refinements with fixed parameters. For **4**·1/2C$_6$H$_6$·1/2C$_6$H$_{14}$, two of the three independent C atoms in solvating hexane were found at two disordered positions with the same occupancies, and the hydrogens of the solvating hexane were not included in the refinements. The Ir-CH hydrogen of the added alkyne was found in the Fourier map, but its position was not refined. One of the two PF$_6$ anions for **9′**·Me$_2$CO occupies two disordered positions with respect to six F atoms in an occupancy ratio of 6:4. The NH hydrogen was located in the Fourier map and was refined isotropically.

Acknowledgment. This work was supported by the JSPS FY2001 “Research for the Future Program”.

Supporting Information Available: Listings of atomic coordinates, anisotropic thermal parameters, and extensive bond lengths and angles for **4**·1/2C$_6$H$_6$·1/2C$_6$H$_{14}$, **5**·MeCN, **7**, and **9′**·Me$_2$CO. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0208117

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