Reactivity of Protons, Tertiary Stannanes, and Alkynes with a Triruthenium Dihydrido Cluster Containing a Face-Capping NHC Ligand

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The triruthenium dihydrido cluster compound [$Ru_3(\mu$-H)$_2(\mu_3$-κ^2-MeImCH)(CO)$_9$] (**1**), which contains a basic face-capping N-heterocyclic carbene ligand (MeImCH) derived from the activation of two C−H bonds of 1,3-dimethylimidazol-2-ylidene (Me$_2$Im), reacts (a) with [HOEt$_2$][BF$_4$] to give a cationic trihydrido cluster; (b) with HSnPh$_3$ and HSnBu$_3$ to give tin-containing triruthenium clusters that arise from the Sn−H oxidative addition of two or three molecules of the tertiary stannane and that contain an Me$_2$Im ligand that is formed by coupling of the CH fragment of the MeImCH ligand of **1** with two hydrido ligands; and (c) with various alkynes to give mixtures of many products. A trinuclear cluster that only contains carbonyl groups and an intact face-capping MeImCH ligand has been isolated from the reaction of **1** with dimethyl acetylenedicarboxylate.

Introduction

After the pioneering work of Lappert and Pye, who reported the synthesis of [Ru$_3$(Et$_2$H$_2$Im)(CO)$_{11}$] (Et$_2$H$_2$Im = 1,3-diethylimidazolin-2-ylidene) in 1977,[1] the N-heterocyclic carbene (NHC) chemistry of transition metal carbonyl clusters has remained asleep for nearly 30 years. The current interest of the chemical community in the coordination chemistry of NHCs[2] and in the catalytic properties of many of their complexes[3] has recently led to the renaissance of the transition metal cluster chemistry of NHCs, to which the research groups of Cole,[4] Whittlesey,[5−7] Clyburne and Cooke,[8−10] and also ourselves[11−16] have importantly contributed.

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Regarding triruthenium clusters containing NHC ligands, Cole et al. have shown that some sulfide-NHC derivatives can be prepared by treating [Ru$_3$(CO)$_{12}$] with 1,3-disubstituted imidazole-2-thiones.[4] Whittlesey et al. have reported that the very bulky carbenes 1,3-di-*tert*-butylimidazol-2-ylidene (^{t}Bu$_2$Im) and 1,3-diadamantylimidazol-2-ylidene (Ad$_2$Im) react with [Ru$_3$(CO)$_{12}$], in 1:1 mol ratio, to give trinuclear CO-substitution products of the type [Ru$_3$(NHC)(CO)$_{11}$], which contain abnormally bound (coordinated through C4) ^{t}Bu$_2$Im[6] and Ad$_2$Im[6,7] as NHC ligands, respectively, and that undergo facile intramolecular C−H bond activation processes upon heating. We have reported that levamisole derivatives can be used to prepare triruthenium clusters with ditopic NHC-thiolate ligands.[11] We have also reported the reactivity of [Ru$_3$(CO)$_{12}$] with a variety of NHCs in 1:1 mol ratio at room temperature, showing that [Ru$_3$(CO)$_{12}$] reacts easily with 1,3-dimethylimidazol-2-ylidene (Me$_2$Im), more slowly with *N*-methyloxazol-2-ylidene (MeOx), and very slowly with 1,3-dimesitylimidazol-2-ylidene (Mes$_2$Im) to give the corresponding normal (NHC coordinated through C2) CO substitution products [Ru$_3$(NHC)(CO)$_{11}$] (NHC = Me$_2$Im, MeOx, Mes$_2$Im).[12] The cluster [Ru$_3$(Me$_2$Im)(CO)$_{11}$] undergoes facile methyl C−H[13−16] and C−N[16] bond activation processes upon heating. Attempts to incorporate more than one NHC ligand to triruthenium clusters by direct treatment of [Ru$_3$(CO)$_{12}$] with NHCs have failed;[4,7] however, the use of imidazole-2-thiones as NHC precursors has allowed the preparation of tri- and tetraruthenium clusters containing two NHC ligands.[4]

With the exception of some thermolysis reactions, commented above,[5,6,13−16] the research activity in the NHC chemistry of ruthenium carbonyl clusters has hitherto been oriented toward

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Scheme 1

Scheme 2
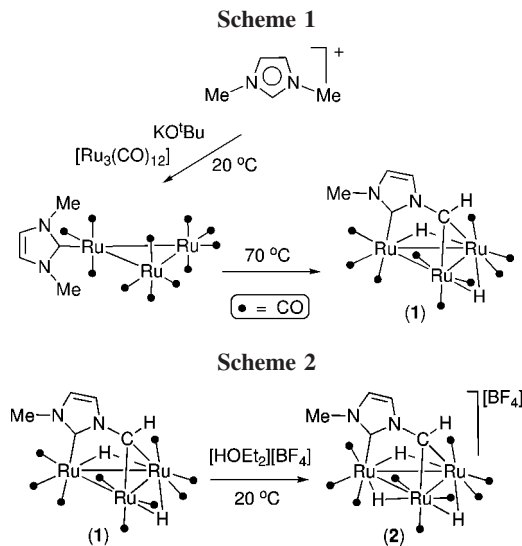
the preparation of NHC-containing products. Therefore, the derivative chemistry of this class of compounds remains unexplored despite the fact that the presence of NHCs in the clusters may confer them unique reactivity properties, as has often been observed for NHC-containing mononuclear complexes.[2,3]

We now report the reactivity of the NHC triruthenium cluster $[Ru_3(\mu\text{-H})_2(\mu_3\text{-}\kappa^2\text{-MeImCH})(CO)_9]$ (**1**; Scheme 1) with $[HOEt_2][BF_4]$, tertiary stannanes, and alkynes. We chose cluster **1** as starting material because (a) it can be easily prepared from $[Ru_3(CO)_{12}]$ and 1,3-dimethylimidazolium salts (Scheme 1),[4] (b) the face-capping coordination of its NHC ligand should prevent cluster fragmentation, and (c) its metal atoms are electron-rich, as a consequence of the high basicity of the NHC ligand. The results are compared with those previously reported for related triruthenium clusters containing no NHC ligands.

Results and Discussion

Reaction of 1 with [HOEt₂][BF₄]. Treatment of a dichloromethane solution of compound **1** with a solution of tetrafluoroboric acid in diethyl ether led to the immediate formation of the pale yellow cationic trihydride $[Ru_3(\mu\text{-H})_3(\mu_3\text{-}\kappa^2\text{-}$ $MeImCH)(CO)_9][BF_4]$ (**2·BF₄**). Its composition was ascertained by microanalysis and mass spectrometry. Its IR spectrum reflects the cationic character of the cluster, displaying the $\nu(CO)$ absorptions at higher wavenumbers than its neutral precursor **1**, as expected for a higher formal oxidation state of the metal atoms. Its ^1H NMR spectrum confirms that the cation has the structure depicted in Scheme 2 because, in addition to the resonances of the bridging organic ligand, it shows two hydride resonances in 2:1 integral ratio, indicating that the cluster contains a symmetry plane.

As far as we are aware, cluster **2** is the first cationic triruthenium trihydride ever reported. Its stability indicates that the Ru atoms of its precursor **1** are basic. No doubt, this is consequence of having a very basic NHC as bridging ligand.[15] Some P- and N-ligand-bridged triruthenium clusters, such as $[Ru_3(\mu\text{-dppm})_2(CO)_8]$[17] (dppm = bis(diphenylphosphanyl)methane) $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Me}_2NNH)(CO)_9]$[18] (Me₂NNH₂ = 1,1-dimethylhydrazine), and $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hampy})(CO)_9]$[19,20] (H₂ampy = 2-amino-6-methylpyridine), can also be protonated
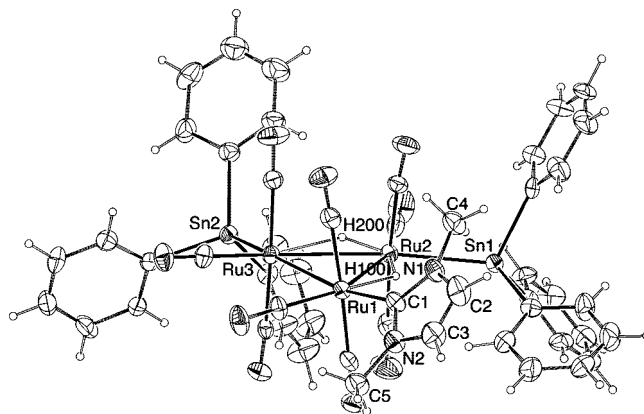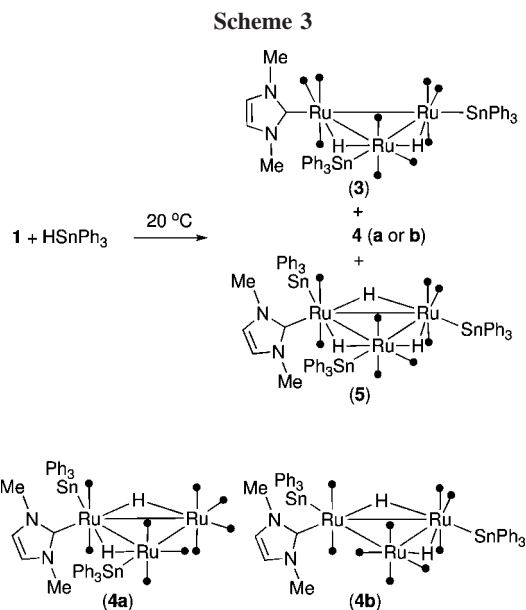

Figure 1. Molecular structure of compound **3**. Selected bond distances (Å): Ru(1)−Ru(2) 3.083(1), Ru(1)−Ru(3) 2.909(1), Ru(2)−Ru(3) 3.058(1), Ru(1)−H(100) 1.81(9), Ru(2)−H(100) 1.64(8), Ru(2)−H(200) 1.49(9), Ru(3)−H(200) 2.09(9), Ru(1)−C(1) 2.14(1), Ru(2)−Sn(1) 2.675(1), Ru(3)−Sn(2) 2.670(1).

Scheme 3

with strong acids in organic solvents to give stable cationic products. However, $[Ru_3(CO)_{12}]$ can only be protonated in neat sulfuric acid to give $[Ru_3(\mu\text{-H})(CO)_{12}]^+$, and it deprotonates in solution in absence of excess acid.[21]

Reactions of 1 with Tertiary Stannanes. Three tin-containing products, namely, two isomers of $[Ru_3(\mu\text{-}$ $H)_2(SnPh_3)_2(Me_2Im)(CO)_9]$ (**3** and **4**) and $[Ru_3(\mu\text{-}$ $H)_3(SnPh_3)_3(Me_2Im)(CO)_8]$ (**5**), were isolated, in yields that depended on the ratio of the reactants, from reactions of compound **1** with triphenylstannane in 1,2-dichloroethane at room temperature (Scheme 3). While the use of an excess of stannane (Sn/Ru₃ > 3) led to a mixture of **3** and **5**, mixtures of **3**, **4**, and **5** with some starting material **1** were formed for Sn/ Ru₃ ≤ 2. In independent experiments, it was confirmed that **4** reacts with triphenylstannane at room temperature to give **5**, while compound **3** is stable under these conditions. No product resulting from the incorporation of only one stannane molecule to the triruthenium cluster was obtained.
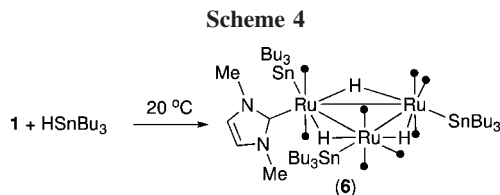
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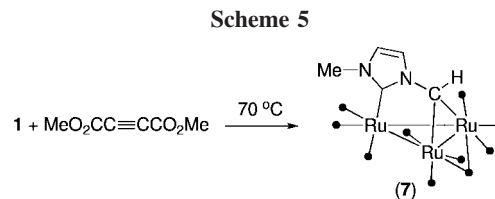
Scheme 4

Scheme 5

The structure of compound **3** was determined by X-ray diffraction (Figure 1). In addition of two equatorial SnPh₃ groups, attached to Ru(2) and Ru(3), and two hydrido ligands, which span the Ru(1)−Ru(2) and Ru(2)−Ru(3) edges and are nearly coplanar with the Ru₃ triangle, compound **3** contains an Me₂Im NHC ligand, occupying an equatorial position of Ru(1), and nine terminal CO ligands.

The room temperature ^{1}H NMR spectrum of **3** indicates that the Me₂Im ligand rotates freely about the Ru−C$_{carbene}$ bond, since only two singlet resonances (at δ 6.80 and 3.51 ppm, with a 1:3 integral ratio) are attributable to the Me₂Im ligand. The hydrides are observed as singlets with satellites, due to coupling with the ^{117}Sn and ^{119}Sn tin isotopes ($J_{117Sn-H} \approx J_{119Sn-H}$).[22] While one hydride (δ −17.39 ppm) contains one pair of satellites (J_{Sn-H} = 40.1 Hz), the other hydride (δ −15.31 ppm) contains two pairs of satellites (J_{Sn-H} = 22.2 and 36.5 Hz). This allows the assignment of the signal at δ −17.39 ppm to the hydride that is *cis* to an SnPh₃ group, H(100) in Figure 1, and the signal at δ −15.31 ppm to the hydride that is *cis* to an SnPh₃ group and *trans* to the other, H(200) in Figure 1. Therefore, in triruthenium cluster chemistry, the *cis*-J_{Sn-H} coupling is greater than the *trans*-J_{Sn-H} coupling.[22]

The composition of compounds **4** and **5** was established by microanalysis and mass spectrometry, the latter showing the corresponding molecular ion. Their ^{1}H NMR spectra indicate the presence of an intact Me₂Im ligand with restricted rotation about the Ru−C$_{carbene}$ bond, since they contain two doublets and two singlets assignable to the protons of the Me₂Im ligands. This suggests the presence of an SnPh₃ group on the same Ru atom as the Me₂Im ligand. In addition to the signals of two (**4**) and three (**5**) SnPh₃ groups, the spectra also contain two (**4**) and three (**5**) hydride resonances. The J_{Sn-H} couplings observed in the hydride satellites of **4** indicate that one hydride is *cis* to an SnPh₃ group and the other is *cis* to one SnPh₃ group and *trans* to the other. The hydride satellites of **5** are broad and ill-resolved.

All these spectroscopic data suggest that the structure of compound **4** is either **4a** or **4b** (Scheme 3) and that the structure of **5** is that depicted in Scheme 3, in which each hydride ligand is *cis* to an SnPh₃ group and *trans* another. This structural assignment is also corroborated by the fact that, (a) in trinuclear clusters, monodentate NHC ligands[5,6,12] and SnR₃ groups[22−25] always occupy equatorial positions, and (b) the oxidative addition of an H-SnR₃ bond to Ru₃ clusters always leads to products with an edge-bridging hydride *cis* to an SnR₃ group.[22−25] The recently reported X-ray structures of [Ru₃(μ-H)₂(SnPh₃)₂(CO)₁₀] and [Ru₃(μ-H)₃(SnPh₃)₃(CO)₉] also support the structures proposed in Scheme 3.[24b]

Only one tin-containing product, [Ru₃(μ-H)₃(SnBu₃)₃(Me₂Im)(CO)₈] (**6**) (Scheme 4), was isolated when compound **1** was treated with tributylstannane, in 1,2-dichloroethane at room temperature, regardless of the ratio of the reactants. The use of Sn/Ru₃ ratios smaller than 3 led to the incomplete consumption of the starting cluster **1**. Its composition was established by microanalysis, mass spectrometry (which gave the corresponding molecular ion isotopomers), and ^{1}H NMR (which indicated the presence of one Me₂Im ligand, three SnBu₃ groups and three hydrides). The pattern of the ν(CO) absorptions of its IR spectrum is very similar to that of complex **5**, confirming that both compounds are isostructural.

Therefore, the oxidative addition of two or more HSnR₃ molecules to compound **1** is accompanied by the reductive coupling of the two hydrides of **1** with the CH fragment of the face-capping MeImCH ligand to give the Me₂Im ligand. Such a ligand transformation has been previously observed studying the reaction of compound **1** with carbon monoxide, which gives [Ru₃(Me₂Im)(CO)₁₁].[13]

Depending on which is the Ru atom of **1** that is attacked by the first HSnPh₃ molecule, different products can be obtained. Compounds **3** and **4** result from the incorporation of two stannane molecules. Compound **3** is formed if the Ru atom attached to the carbene carbon atom of **1** is not attacked by the stannanes. If the first HSnPh₃ molecule attacks this Ru atom, then compounds **4** and **5** are stepwise formed in the presence of more stannane. That compound **3** is not a precursor of the tritin derivative **5** can be explained assuming that the large volume of its Me₂Im ligand impedes the approach of an HSnPh₃ molecule to the NHC-bound Ru atom.

As the SnBu₃ group is smaller and more basic than the SnPh₃ group, the clusters that contain SnBu₃ groups are more susceptible than those containing SnPh₃ groups to react with more stannane molecules. This accounts for the fact that compound **6** is the only product of the reactions of **1** with excess and defect of HSnBu₃, since this implies that the second and third oxidative addition processes have similar or lower energy barriers than the oxidative addition of the first HSnBu₃ molecule. It also explains why a product similar to compound **3** was not obtained in the reaction of **1** with HSnBu₃.

The basicity of the NHC ligand of **1** has to be the responsible for the low activation barriers of these reactions, since it enhances the tendency that the Ru atoms have to get involved in oxidative addition processes. In fact, [Ru₃(CO)₁₂] does not react with tertiary stannanes at room temperature, but gives mono- and binuclear derivatives at high temperatures.[26] The anionic cluster [Ru₃(μ-H)(μ-CO)(CO)₁₀]$^-$ and the activated derivatives [Ru₃(MeCN)(CO)₁₁] and [Ru₃(MeCN)₂(CO)₁₀] oxidatively add tertiary stannanes at room temperature.[23,24]

Reactions of 1 with Alkynes. No reaction was observed when compound **1** was treated with different amounts of phenylacetylene, diphenylacetylene, and dimethyl acetylenedicarboxylate in 1,2-dichloroethane at room temperature. At reflux temperature, phenylacetylene and diphenylacetylene led to mixtures of many unidentified products (at least six colored bands were observed when the reaction mixtures were analyzed by spot TLC). Dimethyl acetylenedicarboxylate also afforded

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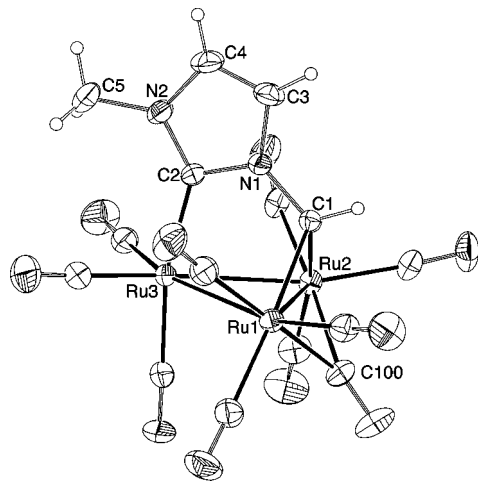
Figure 2. Molecular structure of compound **7**. Selected bond distances (Å): Ru(1)−Ru(2) 2.7442(5), Ru(1)−Ru(3) 2.8392(5), Ru(2)−Ru(3) 2.8282(5), Ru(1)−C(1) 2.150(4), Ru(2)−C(1) 2.132(5), Ru(3)−C(2) 2.083(5), Ru(1)−C(100) 2.125(5), Ru(2)−C(100) 2.162(5).

a mixture of compounds, but a major product, subsequently isolated in 27% yield and identified as [Ru$_3$(μ_3-κ^2-MeImCH)(μ-CO)(CO)$_9$] (**7**), was formed in this occasion (Scheme 5). A GC analysis of the reaction solution revealed the presence of dimethyl maleate.

The structure of compound **7** was determined by X-ray diffraction (Figure 2). With respect to compound **1**, compound **7** maintains the face capping MeImCH ligand and three terminal CO groups per metal atom, but a new CO ligand, which formally replaces the two hydrides of compound **1**, spans the Ru(1)−Ru(2) edge. This bridging CO ligand is clearly observed in the IR spectrum of compound **7** as a medium-intensity band at 1854 cm^{-1}.

It seems that, in the reaction that leads to compound **7**, the alkyne is hydrogenated with the hydrides of compound **1** and that the resulting trinuclear species prefers to alleviate its unsaturation taking a CO molecule from the reacting solution (it should arise from concomitant CO-substitution processes) rather than coordinating the resulting alkene molecule. As stated above, the reaction is not selective, since TLC revealed that the reaction solution also contained small amounts of many other unidentified metal-containing products.

As far as we are aware, no reactions of alkynes with triruthenium dihydrides have been reported. The monohydrides [Ru$_3$(μ-H)(μ_3-κ^2-Me$_2$NNH)(CO)$_9$][27] and [Ru$_3$(μ-H)(μ_3-κ^2-Hampy)-(CO)$_9$],[28] which also have face-capping ligands, react with alkynes to give alkenyl cluster derivatives.

Concluding Remarks. The basic NHC ligand MeImCH of cluster **1** enhances the reactivity of this cluster, as compared with that of [Ru$_3$(CO)$_{12}$]. While cluster **1** is easily protonated to give selectively the cationic trihydride **2**, its reactions with tertiary stannanes and alkynes are not selective, giving mixtures of products. It reacts easily with tertiary stannanes to give cluster derivatives (**3-6**) that arise from the oxidative addition of the Sn−H bond of the reagents and from the transformation of the face-capping MeImCH ligand into a terminal Me$_2$Im ligand. Compound **7**, the only cluster product isolated from the reactions of compound **1** with alkynes, contains an intact face-capping MeImCH ligand and no hydrides.

Experimental Section

General Data. Compound **1** was prepared by a published method.[14] The remaining reagents were purchased from commercial suppliers. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) or CaH$_2$ (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen before use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^{1}H NMR spectra were run on a Bruker DPX-300 instrument, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$). Microanalyses were obtained from the University of Oviedo Analytical Service. FAB mass spectra were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer. GC analyses were performed on a Perkin-Elmer 8600 gas chromatograph, equipped with a 12-m AQ2 capillary column and a flame ionization detector.

Reaction of 1 with [HOEt$_2$][BF$_4$]. A 54% solution of tetrafluoroboric acid in diethyl ether (6 μL, 0.072 mmol) was added to a solution of complex **1** (40 mg, 0.061 mmol) in dichloromethane (10 mL). The color changed from orange to pale yellow. The solvent was removed at reduced pressure and the residue was triturated and washed with diethyl ether (3 × 5 mL) to give [Ru$_3$(μ-H)$_3$(μ_3-κ^2-MeImCH)(CO)$_9$][BF$_4$] (**2**·BF$_4$) as a pale yellow solid (30 mg, 68%). Anal. calcd for C$_{14}$H$_9$BF$_4$N$_2$O$_9$Ru$_3$ (739.24): C, 22.75; H, 1.23; N, 3.79. Found: C, 22,70; H, 1.17; N 3.74. (+)-FAB MS: *m/z* 653 [*M* - BF$_4$]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2168 (w), 2138 (m), 2114 (m), 2101 (vs), 2083 (m), 2051 (s). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.13 (d, $J = 1.9$ Hz, 1 H, CH), 7.08 (s, 1 H, CH), 6.76 (d, $J = 1.9$ Hz, 1 H, CH), 3.69 (s, 3 H, Me), −12.0 (s, 1 H, μ-H), −18.87 (d, $J = 1.9$ Hz, 2 H, μ-H).

Reaction of 1 with Triphenylstannane. Solid triphenylstannane (84 mg, 0.239 mmol) was added to a solution of compound **1** (50 mg, 0.082 mmol) in 1,2-dichloroethane (20 mL). After stirring for 20 min at room temperature, the color changed from orange to bright red. The solvent was removed under reduced pressure and the reaction mixture was separated on TLC plates (silica gel). Hexane eluted a small amount of **1**. Hexane/dichloromethane/diethyl ether (7:1:1) eluted three bands. The first one, yellow, contained [Ru$_3$(μ-H)$_2$(SnPh$_3$)$_2$(Me$_2$Im)(CO)$_9$] (**4**) (12 mg, 12%). The second one, yellow, contained [Ru$_3$(μ-H)$_3$(SnPh$_3$)$_3$(Me$_2$Im)(CO)$_8$] (**5**) (10 mg, 8%). The thirth one, red, contained [Ru$_3$(μ-H)$_2$(SnPh$_3$)$_2$(Me$_2$Im)(CO)$_9$] (**3**) (30 mg, 29%). Longer reaction times, maintaining the ratio of the reagents gave more of **5** and less of **4**.

Data for 3: Anal. calcd for C$_{50}$H$_{40}$N$_2$O$_9$Ru$_3$Sn$_2$ (1353.51): C, 44.37; H, 2.98; N, 2.07. Found: C, 44.35; H, 2.97; N 2.06. (+)-FAB MS: *m/z* 1325 [*M* - CO]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2062 (m), 2027 (vs), 1992 (m), 1984 (m). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.69 (m, 5 H, CH), 7.31 (m, 25 H, CH), 6.80 (s, 2 H, CH), 3.51 (s, 6 H, Me), −15.31 (s, sat, $J_{H-Sn} = 36.5, 22.2$ Hz, 1 H, μ-H), −17.39 (s, sat, $J_{H-Sn} = 40.1$ Hz, 1 H, μ-H).

Data for 4: Anal. calcd for C$_{50}$H$_{40}$N$_2$O$_9$Ru$_3$Sn$_2$ (1353.49): C, 44.37; H, 2.98; N, 2.07. Found: C, 44.41; H, 3.10; N 2.14. (+)-FAB MS: *m/z* 1296 [*M* − 2 CO]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2104 (m), 2050 (s), 2038 (sh), 2026 (vs), 1976 (m), 1960 (m). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.73 (m, 6 H, CH), 7.36 (m, 25 H, CH), 6.82 (d, $J = 1.6$ Hz, 1 H, CH), 6.60 (d, $J = 1.6$ Hz, 1 H, CH), 3.32 (s, 3 H, Me), 3.27 (s, 3 H, Me), −15.95 (d, sat, $J_{H-H} = 2.1$ Hz, $J_{H-Sn} = 35.3, 25.4$ Hz, 1 H, μ-H), −16.55 (d, sat, $J_{H-H} = 2.1$ Hz, $J_{H-Sn} = 21.5$ Hz, 1 H, μ-H).

Data for 5: Anal. calcd for C$_{67}$H$_{56}$N$_2$O$_8$Ru$_3$Sn$_3$ (1676.51): C, 48.00; H, 3.37; N, 1.67. Found: C, 47.98; H, 3.36; N 1.66. (+)-FAB MS: *m/z* 1678 [*M*]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2103 (w), 2077 (m), 2031 (vs), 1959 (m). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.50 (m, 45 H,

CH), 6.76 (d, J = 1.9 Hz, 1 H, CH), 6.58 (d, J = 1.9 Hz, 1 H, CH), 3.51 (s, 3 H, Me), 3.29 (s, 3 H, Me), −13.98 (d, br sat, J_{H-H} = 1.5 Hz, 1 H, μ-H), −14.83 (m, 2 H, μ-H).

Reaction of 1 with Tributylstannane. A solution of compound **1** (40 mg, 0.062 mmol) and tributylstannane (33 μL, 97%, 0.121 mmol) in 1,2-dichloroethane (20 mL) was stirred at room temperature for 30 min. The color changed from orange to bright red. The solvent was removed under reduced pressure and the reaction mixture was separated on TLC plates (silica gel). Hexane eluted a small amount of **1**. Hexane/dichloromethane (3:1) eluted several bands. The first and major one, yellow, contained [Ru₃(μ-H)₃(SnBu₃)₃(Me₂Im)(CO)₈] (**7**) (25 mg, 60%). Anal. Calcd for C₄₉H₉₂N₂O₈Ru₃Sn₃ (1496.60): C, 39.32; H, 6.20; N, 1.87. Found: C, 39.27; H, 6.26; N 1.83. (+)-FAB MS: m/z 1439 [M - Bu]⁺. IR (CH₂Cl₂): ν_{CO} 2100 (w), 2060 (m), 2020 (vs), 1940 (m). ¹H NMR (CDCl₃, 293 K): δ 6.90 (s, 2 H, CH), 4.09 (s, 3 H, Me), 4.07 (s, 3 H, Me), −13.66 (d, sat, J_{H-H} = 2.1 Hz, J_{H-Sn} = 35.4, 25.9 Hz, 1 H, μ-H), −14.41 (d, sat, J_{H-H} = 2.1 Hz, J_{H-Sn} = 32.9 Hz, 1 H, μ-H), −16.55 (s, sat, J_{H-Sn} = 34.2 Hz, 1 H, μ-H).

Reaction of 1 with Dimethyl Acetylenedicarboxylate. A solution of compound **1** (40 mg, 0.062 mmol) and dimethyl acetylenedicarboxylate (17 mg, 0.121 mmol) in 1,2-dichloroethane (10 mL) was stirred at reflux temperature for 2 h. A GC analysis of the reaction solution revealed the presence of dimethyl maleate. Silica gel (ca. 2 g) was added and the solvent was evaporated under reduced pressure. The solid residue was placed onto a silica gel chromatography column (25 × 3 cm) packed in hexane. Hexane eluted a small amount of compound **1**. Hexane/dichloromethane (8:1) eluted several bands. The first and major band, red, contained [Ru₃(μ_3-κ^2-MeImCH)(μ-CO)(CO)₉] (**7**) (13 mg, 27%). Anal. calcd for C₁₅H₆N₂O₁₀Ru₃Sn₃ (677.43): C, 26.59; H, 0.89; N, 4.14. Found: C, 26.64; H, 0.93; N 4.09. (+)-FAB MS: m/z 679 [M]⁺. IR (CH₂Cl₂): ν_{CO} 2082 (m), 2043 (vs), 2034 (s), 2008 (s), 1996 (s), 1989 (sh), 1854 (m, br). ¹H NMR (CDCl₃, 293 K): δ 7.29 (s, 1 H, CH), 7.21 (d, J = 1.5 Hz, 1 H, CH), 6.61 (d, J = 1.5 Hz, 1 H, CH), 3.85 (s, 3 H, Me).

X-Ray Diffraction Analyses. Diffraction data were collected on a Nonius Kappa-CCD diffractometer equipped with a 95 mm CCD camera and a κ-goniostat, using graphite-monochromated Cu Kα radiation. Empirical or semiempirical absorption corrections were applied using SORTAV[29] (**3**) or XABS2[30] (**7**). Structures were solved by Patterson interpretation using the program DIRDIF-96.[31] Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL-97.[32] All non-H atoms of all structures were refined anisotropically. Hydrogen atoms H100 and H200 of **3** were located in the corresponding Fourier maps and refined without restrictions. The remaining hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The molecular plots were made with the PLATON program package.[33] The WINGX program system[34] was used throughout the structure determinations. Selected crystal data for **3**: C₅₀H₄₀N₂O₉Ru₃Sn₂, M_r = 1353.51, crystal dimensions: 0.10 × 0.05 × 0.02, monoclinic, space group $P2_1/c$, a = 19.9871(5) Å, b = 9.5179(3) Å, c = 28.4447(7) Å, β = 98.785(3)°, V = 5077.8(2) Å³, Z = 4, ρ_{calcd} = 1.770 g cm⁻³, $F(000)$ = 2632, μ = 15.227 mm⁻¹, 56516 independent reflections, R_1 = 0.0546, wR_2 = 0.1317 (all data). Selected crystal data for **7**: C₁₅H₆N₂O₁₀Ru₃, M_r = 677.43, crystal dimensions: 0.17 × 0.07 × 0.03, monoclinic, space group $P2_1/n$, a = 12.4159(4) Å, b = 9.9250(3) Å, c = 16.3455(6) Å, β = 98.785(3)°, V = 2009.65(12) Å³, Z = 4, ρ_{calcd} = 2.239 g cm⁻³, $F(000)$ = 1288, μ = 18.558 mm⁻¹, 23622 independent reflections, R_1 = 0.0398, wR_2 = 0.1011 (all data). CCDC deposition numbers: 710571 (**3**) and 710572 (**7**).

Supporting Information Available: Crystallographic data in CIF format of the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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