Os(H)(Cl)(CO)(PPh3)2, Rh(COD)(PPh3)2, and Cp*Rh(NCMe)3. In fact, the Cp*Rh(NCMe)3-catalyzed deuteriation of BT gives specifically the cis-dideuteriobenz(b) thiophene; this is the stereochemistry predicted by the mechanism in Scheme III. Thus, the mechanism that was proposed for this reaction by Fish and co-workers is supported by the results of our rhenium studies reported herein, which show that 2,3-MeBT gives the amount of the 2,3-η2 form. On an HDS catalyst, a trend can be readily explained by the results of our experiments withMe-substituted (2,3-η2)-BT.

The olefin hydrogenation mechanism is also likely to be involved in the conversion of BT to DHBT in heterogeneous catalysts. It allows one to account for the relative rates of hydrogenation and HDS of methyl-substituted rhodium catalysts. These rates decrease with increasing methyl substitution in the order BT > 2-MeBT > 3-MeBT > 2,3-MeBT. This trend can be readily explained by the results of our rhenium studies reported herein, which show that 2,3-methyl substitution favors η1(S)-BT coordination and decreases the rates of hydrogenation and HDS of methyl-substituted BT. It is also evident that this factor is involved in the conversion of BT to DHBT on heterogeneous catalysts. It allows one to account for the relative rates of hydrogenation and HDS of methyl-substituted BT.

Incorporation of Tributylsilyl and Trialkylstannyl Groups into Ruthenium Carbonyl Clusters. Carboxyl Substitution versus Trialkylsilane or Trialkylstannane Elimination in These Clusters

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The clusters [Ru3(μ-H)(μ-η2-ampy)(PPh3)(CO)6] (n = 0 (1), 1 (2), 2 (3); Hampy = 2-amino-6- methylpyridine) react with HSiEt3 to give the oxidative substitution products [Ru3(μ-H)(μ-η4-ampy) (SiEt3)(PPh3)(CO)6] (n = 0 (4a), 1 (5a), 2 (6a)). Similar reactions of 1-3 with HSnBu3 afford [Ru3(μ- H)(μ-η2-ampy)(SnBu3)(PPh3)(CO)6] (n = 0 (4b), 1 (5b), 2 (6b)). In all cases, (a) the added hydride spans a metal-metal edge adjacent to that supported by the bridging amido group, (b) the SiEt3 or SnBu3 ligands occupy an equatorial site on the Ru atom bound to the two hydrides, being trans to the hydride which spans the same edge as the amido group, and (c) in the compounds containing PPh3 ligands, these ligands occupy equatorial positions, cis to hydrides, on the Ru atoms bound to only one hydride. The reactions of 4a and 5a with PPh3 produce the elimination of HSiEt3, rendering the complexes 2 and 3, respectively; however, similar reactions of the tin-containing compounds 4b and 5b afford the substitution products 5b and 6b, respectively. The compounds have been characterized by infrared and 1H, 13C, and 11P NMR spectroscopies and, in the case of 4a by X-ray diffraction. Crystal data for 4a: monoclinic, space group P21/n, a = 10.849 (8) Å, b = 20.809 (4) Å, c = 12.049 (8) Å, β = 98.21 (5)°, V = 2692 (2) Å3, Z = 4, μ(Mo Kα) = 17.17 cm−1, R = 0.048, Rw = 0.053 for 2036 reflections and 287 variables.

Introduction

Organosilanes and organostannanes are widely used in metal-catalyzed hydrosilylation and hydrostannation reactions. However, little attention has been paid to metal carbonyl clusters as catalyst precursors in such reactions.2-4 Concerning ruthenium, the trinuclear clusters [Ru6(μ3-CO)12] and [Ru6(μ3-H)(CO)12] have been reported as catalyst precursors for the dehydrogenative silylation and hydrostannation of olefins, respectively. In the latter process, the anionic cluster [Ru6(μ3-H)(CO)11]2− reacts with triethylaline to give the trinuclear derivative [Ru3(μ-H)-]


Ruthenium Carbonyl Clusters

however, the reactions of \([\text{Ru}(\text{CO})_\text{Cl}])\) with trialkylsilanes have been shown to lead to the break up of the trinuclear structure, affording bi- and mononuclear derivatives.\(^5\) A very recent report has provided examples of trialkoxysilyl groups attached to triosmium clusters, showing that the alkoxy fragments can coordinate to metals through their oxygen atoms, i.e. as in \([\text{Os}_3(\mu-\text{H})_3(\mu_3-\text{η}^2-\text{ampy})(\text{CO})_3]^{7\text{a}}\).\(^6\)

We now report some examples of trialkylsilyl and trialkylstannyl ligands coordinated to neutral ruthenium clusters. We also describe some reactions which prove that hydrido-stannyl complexes are more stable than hydrido-silyl derivatives toward the elimination of trialkylstannane or trialkylsilane. As a starting ruthenium carbyl cluster, we have used the complex \([\text{Ru}_3(\mu-\text{H})_3(\mu_3-\text{η}^2-\text{ampy})(\text{CO})_3]^{7\text{a}}\) \((1)\) (Hampy = 2-amino-6-methylpyridine) because, as reported in previous works,\(^7\)\(^1\)\(^2\) the face-bridging ampy ligand has proved to hold the metal atoms firmly, preventing cluster degradation. The products have been characterized by \(^1\)H, \(^13\)C, and \(^{31}\)P NMR spectroscopies and other analytical methods and, in one case (namely, the cluster \([\text{Ru}_3(\mu-\text{H})_3(\mu_3-\text{η}^2-\text{ampy})(\text{SiEt}_3)](\text{CO})_3])\) by a crystal structure determination.


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**Table I. Selected IR Data**

<table>
<thead>
<tr>
<th>compd</th>
<th>(v(\text{CO}) \text{ cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a 2080 (s), 2047 (vs), 2017 (vs), 1999 (s), 1987 (m), 1961 (m)</td>
<td></td>
</tr>
<tr>
<td>4b 2080 (s), 2048 (vs), 2012 (vs), 2000 (m, sh), 1983 (m), 1948 (m)</td>
<td></td>
</tr>
<tr>
<td>5a 2058 (vs), 2009 (vs), 2002 (vs), 1986 (m), 1944 (a)</td>
<td></td>
</tr>
<tr>
<td>5b 2060 (s), 2009 (vs, br), 1999 (s, sh), 1987 (m), 1972 (w, sh), 1942 (s)</td>
<td></td>
</tr>
<tr>
<td>6a 2021 (s), 2002 (vs), 1978 (m), 1946 (s), 1937 (m)</td>
<td></td>
</tr>
<tr>
<td>6b 2020 (s), 1997 (vs), 1980 (m), 1951 (m), 1933 (m)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) In THF solution. Abbreviations are as follows: s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder.

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**Figure 1. ORTEP drawing of \([\text{Ru}_3(\mu-\text{H})_3(\mu_3-\text{η}^2-\text{ampy})(\text{SiEt}_3)](\text{CO})_3])\) (4a) with atoms shown as 30% probability ellipsoids. C18 and C18P are the two statistically occupied sites for this methyl group.**

The potential applications of the compounds described herein as catalyst precursors in reactions involving silanes, stannanes, and organic substrates are currently under investigation in our laboratories.

**Results and Discussion**

**Synthesis and Spectroscopic Characterization.** The pale-yellow, air-stable, trinuclear cluster \([\text{Ru}_3(\mu-\text{H})_3(\mu_3-\text{η}^2-\text{ampy})(\text{SiEt}_3)](\text{CO})_3]) (4a) (Scheme I) could be efficiently prepared by treatment of \([\text{Ru}_3(\mu-\text{H})_3(\mu_3-\text{η}^2-\text{ampy})(\text{CO})_3]) (1) with HSiEt₃. Although the reaction proved to be very slow at room temperature, it was complete within minutes in refluxing THF, dichloromethane, or 1,2-dichloroethane. Its IR spectrum (Table I) shows the \(v(\text{CO})\) absorptions slightly shifted to higher wavenumbers than those of complex 1, as expected for a higher formal oxidation state of the metal atoms. Its \(^1\)H NMR (Table II) clearly indicates the incorporation of a new hydride and one SiEt₃ group to the original cluster. The number of CO ligands was evident from the \(^13\)C(\(^1\)H) NMR spectrum (Table III), which shows eight CO resonances, three of which split with considerable coupling constants in the proton-coupled \(^13\)C NMR spectrum (Table III). These data indicate that only three CO ligands are trans to hydride and, therefore, the SiEt₃ group should be in an equatorial site of the cluster in a position trans to a hydrido ligand. With all these data it was not possible to precisely locate the SiEt₃ group in the cluster, and thus, an X-ray structure determination (Figure 1), which is discussed below, was carried out.
The activity and selectivity of homogeneous catalysts are in many cases enhanced by the presence of phosphine ligands. Thus, we were interested in knowing whether phosphine-substituted derivatives of 1 would behave in the same way as complex 1 in their reactions with triethylsilane.

The cluster [Ru$_3$(µ-H)$_3$(µ$_3$η$_3$-ampy)(PPh$_3$)(CO)$_2$] (2) reacted with HSiEt$_3$ to give [Ru$_3$(µ-H)$_3$(µ$_3$η$_3$-ampy)-(SiEt$_3$)(PPh$_3$)(CO)$_2$] (5a) in high yield. The structure we propose for this complex (Scheme I) is based on its spectroscopic data (Tables I–III). Particularly, the carbonyl region of the proton-coupled and proton-decoupled $^{13}$C NMR spectra (Figure 2) strongly supports that the coordination sites occupied by the PPh$_3$ ligand in 2 and the SiEt$_3$ group in 4a are maintained in 5a. The proton-decoupled spectrum shows three doublets, one with a large coupling constant (17.0 Hz), which we have assigned to

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**Table II. Selected $^1$H and $^{31}$P($^1$H) NMR Data**

<table>
<thead>
<tr>
<th>compd</th>
<th>H$^1$</th>
<th>H$^2$</th>
<th>H$^3$</th>
<th>NH</th>
<th>Me</th>
<th>µ-H</th>
<th>δ($^1$P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>6.69 (d)</td>
<td>7.19 (t)</td>
<td>6.65 (d)</td>
<td>3.28 (s)</td>
<td>2.29 (s)</td>
<td>-0.64 (s)</td>
<td>11.96 (s)</td>
</tr>
<tr>
<td>4b</td>
<td>6.70 (d)</td>
<td>7.15 (t)</td>
<td>5.12 (d)</td>
<td>3.42 (s)</td>
<td>2.04 (s)</td>
<td>-0.78 (s, sat)</td>
<td>-11.39 (s, sat)</td>
</tr>
<tr>
<td>5a</td>
<td>6.50 (d)</td>
<td>7.16 (t)</td>
<td>5.70 (d)</td>
<td>d</td>
<td>2.60 (d)</td>
<td>-0.50 (d, 3.4)</td>
<td>11.20 (d)</td>
</tr>
<tr>
<td>5b</td>
<td>5.91 (d)</td>
<td>6.52 (d)</td>
<td>5.57 (d)</td>
<td>d</td>
<td>1.99 (s)</td>
<td>-0.50 (d, sat)</td>
<td>11.42 (d, sat)</td>
</tr>
<tr>
<td>6a</td>
<td>5.96 (d)</td>
<td>6.67 (t)</td>
<td>5.82 (d)</td>
<td>2.57 (d)</td>
<td>[5.0]</td>
<td>2.08 (s)</td>
<td>-7.62 (s, 6.0)</td>
</tr>
<tr>
<td>6b</td>
<td>5.88 (d)</td>
<td>6.69 (t)</td>
<td>5.74 (d)</td>
<td>2.83 (d)</td>
<td>[5.9]</td>
<td>1.99 (s)</td>
<td>-5.32 (s, 5.3)</td>
</tr>
</tbody>
</table>

* Spectra recorded at 300 MHz ($^1$H) or 121.7 MHz ($^{31}$P), 25 °C; chemical shifts (δ, ppm) relative to SiMe$_4$ (internal, $^1$H) or 85% H$_3$PO$_4$ (external, $^{31}$P); multiplicities (s = singlet, d = doublet, t = triplet, sat = with tin satellites) in parentheses; coupling constants (Hz) in brackets $[^1$H-H$]$ or braces $[^1$H-P$]$; coupling constants $^{31}$P-H$^1$ for H$^1$, H$^2$, and H$^3$ are of ca. 7.4 Hz in all cases. The $^1$H resonances of the SiEt$_3$, SnBu$_3$, and PPh$_3$ ligands, although confirming the presence of these ligands in the clusters, are noninformative multiplets. * In CD$_2$Cl$_2$. * In C$_6$H$_5$. * Unobserved.

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**Table III. Selected $^{13}$C NMR Data**

<table>
<thead>
<tr>
<th>compd</th>
<th>δ(CO)</th>
<th>δ(ampy)</th>
<th>δ(SiEt$_3$ or SnBu$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>202.6 (d)</td>
<td>[27.5]</td>
<td>202.3, 200.0 (d) [4.6], 197.6 (d) [4.8], 196.8 (d) [20.1], 193.3 (d) [9.6], 189.0 (d) [5.2], 184.7</td>
</tr>
<tr>
<td>4b</td>
<td>202.9 (d) [25.0], 202.7, 200.0 (d) [4.2], 197.1 (d) [5.6], 196.4 (d) [18.7], 193.9 (d) [10.6], 189.1 (d) [5.3], 183.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>206.1 (d) [18.9], 205.8 (dd) [8.4], 203.8, 199.9 (dd) [16.8]</td>
<td>179.7, 159.9, 139.2, 119.6, 111.5, 30.1</td>
<td>30.5, 28.0, 13.8, 13.3</td>
</tr>
<tr>
<td>5b</td>
<td>206.0 (dd) [8.3], 205.7 (d) [16.5], 203.4, 199.7 (dd) [15.3]</td>
<td>179.7, 159.6, 138.2, 118.3, 110.7, 30.1</td>
<td>30.1, 27.9, 13.6, 12.6</td>
</tr>
<tr>
<td>5b</td>
<td>206.1 (d) [18.1], 207.3 (dd) [5.0], 204.9, 203.5 (br), 201.1 (dd) [15.0]</td>
<td>180.8, 160.8, 137.4, 117.8, 110.4, 30.0</td>
<td>30.2, 28.0, 13.8, 12.1</td>
</tr>
</tbody>
</table>

* In order to assign all types of couplings, the spectra (CD$_2$Cl$_2$, 75.5 MHz, 25 °C) were recorded in both proton-decoupled and proton-coupled modes; the data given for the carbonyl resonances correspond to the proton-coupled spectra, the other ones are proton decoupled. The resonances of the PPh$_3$ ligands have not been included. Chemical shifts (δ, ppm) are relative to internal SiMe$_4$. Unless otherwise stated all resonances are singlets; other multiplicities are given in parentheses; coupling constants (Hz) are given in brackets $[^1$C-$^1$H$]$ or braces $[^1$C-$^3$P$]$. The compound 5a is not soluble enough to allow spectra to be taken.
These data strongly support that upon reaction with silane, the results contrast with those reported for the atoms would give a much smaller coupling constant. The moves from its original position to that shown in Scheme tin-containing derivatives of their
different metal atoms. The high chemical shift of the equatorial carbonyl E in compound 5a must be due to the presence of the two hydrides and the SiEt$_3$ group on the same ruthenium atom.

The bi(triphenylphosphine) complex [Ru$_3$(μ-H)$_2$(μ$_3$η$_2$-ampy)](PPh$_3$)$_6$(CO)$_6$ (3) also reacted smoothly with HSiEt$_3$ to give [Ru$_3$(μ-H)$_2$(μ$_3$η$_2$-ampy)](PPh$_3$)$_6$(CO)$_6$ (6a). The $^1$H and $^{31}$P NMR spectra were particularly useful to propose a structure for this complex. The two hydride resonances of the proton spectrum are coupled to both phosphorus atoms, but the coupling constants are very small (Table II), indicating none of the PPh$_3$ ligands is trans to hydrides. The $^{31}$P($^1$H) NMR spectrum consists of an AX spin system with a coupling constant of 56.5 Hz, typical of two phosphine ligands in a linear arrangement along a metal-metal bond; any other arrangement of two phosphine ligands on different metal atoms would give a much smaller coupling constant.

These results strongly support that upon reaction with HSiEt$_3$, one of the two phosphine ligands of complex 3 moves from its original position to that shown in Scheme. A related coordination shift of PPh$_3$ ligand has been reported previously on protonation of complex 3 with HBO$_4$ to give [Ru$_3$(μ-H)$_2$(μ$_3$η$_2$-ampy)](PPh$_3$)$_6$(CO)$_6$BF$_4$.$^{10}$

In all these reactions only 1 equiv of HSiEt$_3$ was incorporated into the clusters, even using a large excess of silane. These results contrast with those reported for the anionic complex [Ru$_3$(μ-H)$_2$(μ$_3$η$_2$-ampy)](PPh$_3$)$_6$(CO)$_6$,$^{11}$ which reacts with 2 equiv of HSiEt$_3$ to give hydrogen and the bi-siP$_2$ derivative $^{12}$ (Ru$_3$(μ-H)(μ$_3$η$_2$-ampy))(PPh$_3$)$_6$(CO)$_6$. The reactions of compounds 1–3 with HSiBu$_3$ gave the tin-containing derivatives [Ru$_3$(μ-H)$_2$(μ$_3$η$_2$-ampy)](SnBu$_3$)(PPh$_3$)$_6$(CO)$_6$$_n$ (n = 0 (4b), 1 (5b), 2 (6b)) (Scheme II). Their IR and NMR spectra (Tables I–III) are nearly identical to those of the silicon-containing compounds described above, indicating that they have analogous structures. Interestingly, both hydride resonances of their $^1$H NMR spectra show satellites due to coupling to $^{119}$Sn and $^{117}$Sn, as expected for hydrides bound to the same ruthenium atom as the SnBu$_3$ group. Also, the resonances of the $^{31}$P NMR spectra do not contain any satellite, suggesting that the phosphine ligands are bound to ruthenium atoms different to that attached to the SnBu$_3$ group. These data also support the structures we propose for both the silicon- and tin-containing compounds.

Elimination of HSiEt$_3$ or HSiBu$_3$ versus CO Substitution Reactions. To compare the reactivity of the silicon-containing versus the tin-containing complexes, the reactions of triphenylphosphine with all compounds described herein were investigated.

As depicted in Scheme I, the reactions of 4a and 5a with PPh$_3$ produced the elimination of HSiEt$_3$, giving 2 and 3, respectively. However, similar reactions with the tin-containing compounds 4b and 5b afforded the carbonyl substitution products 5b and 6b, respectively (Scheme II). Moreover, complex 4b did not react with carbon monoxide (1 atm, refluxing toluene) and complex 6b did not react with triphenylphosphine even in refluxing toluene, whereas complex 4a gave complex 1 upon treatment with carbon monoxide (1 atm) at room temperature and complex 6a gave a mixture of unidentified products upon reaction with triphenylphosphine in refluxing toluene. These reactions demonstrate that the hydrido–stanny derivatives are much more stable than the hydrido–silyl derivatives toward the elimination of trialkylstannane or trialkylsilane.

From a mechanistic point of view, the mild conditions under which many of the reactions described in this and other works take place suggest that a low-energy path is being used in the transformations. As indicated by Lavigne et al. in related (phenyl(2-pyridyl)amido)ruthenium carbonyl clusters,$^{13}$ the opening of one of the Ru−N arms of the amido bridge would provide a reactive coordinatively unsaturated 46-electron species as a low-energy transition state. Although we have not observed such a bridge opening in any of our neutral complexes containing ampy as a μ$_3$η$_2$-ligand, it has been observed by others in related anionic complexes; i.e., the complex PP(N[Ru$_3$(μ$_3$η$_2$-N(PPh)(C$_6$H$_5$N))(CO)$_6$ reacts reversibly with carbon monoxide to give PP[N[Ru$_3$(μ$_3$η$_2$-N(PPh)(C$_6$H$_5$N))(CO)$_6$] in which the amido group is bound to only one ruthenium atom.$^{14}$

Structural Characterization of [Ru$_3$(μ-H)$_2$(μ$_3$η$_2$-ampy)](SiEt$_3$)(CO)$_6$ (4a). The X-ray structure of 4a has been determined by X-ray diffraction (Figure 1). A selection of bond distances and angles is given in Table IV. The cluster consists of a triangle of ruthenium atoms.
The clusters 1, 2, 3, 4, and 5 were prepared using techniques and were monitored by solution IR spectroscopy (Tables I, II, and III) were added to a solution of complex 1 (149 mg, 0.221 mmol) in 1,2-dichloroethane (8 mL). The initial orange solution was refluxed until the color turned pale-yellow (7 min). The solvent was then evaporated again to dryness to give complex 4a as a yellow solid (152 mg, 93%). Anal. Calcd for C64H39N3O23P8: C, 51.87; H, 4.90; N, 2.07. Found C, 51.80; H, 4.87; N, 2.06.

Reaction of Complex 4a with Triphenylphosphine. A solution of complex 4a (41 mg, 0.056 mmol) in THF (10 mL) was treated with PPh3 (15 mg, 0.057 mmol). After 1 h, the IR spectrum of the solution indicated that it only contained the complex 2.

Reaction of Complex 5a with Triphenylphosphine. A solution of complex 5a (4 mg, 0.009 mmol) in THF (4 mL) was treated with PPh3 (3.3 mg, 0.013 mmol). After stirring for 2 h at room temperature, the reaction was complete (IR). It was then heated at reflux temperature for 2 min, when the IR spectrum showed the complete transformation of 5a into 1.

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Ruthenium Carbonyl Clusters

The measurement of dimensions were determined by least-squares refinement from difference syntheses and was refined by weighted anisotropic full-matrix.

The crystal data

286

Collected up to 286 (IR absorption). The crystal data were taken from ref 18. The drawing was made with ORTEP.19 All calculations were performed on a MicroVAX 3100 computer using the SDP program package.30 Selected bond lengths and angles are given in Table IV; positional atomic coordinates are given in Table VI.

Acknowledgment. We are grateful to the CICYT (Spain) (Project No. MAT90-0173) and the CNRS (France) for support of this work. We also thank the FICYT (Asturias, Spain) for a postgraduate scholarship to A.L. and Dr. G. Lavigne (CNRS, Toulouse, France) for a preprint copy of ref 8b.

Supplementary Material Available: For 4a, tables of thermal parameters for the non-hydrogen atoms, bond lengths, bond angles, and H-atom coordinates (4 pages). Ordering information is given on any current masthead page.

OM920004F


