Alkyne, Triorganosilyl, and Triorganostannyl Derivatives of Anionic Triruthenium Carbonyl Cluster Complexes Containing Bridging Pyrazolyl Ligands

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The anionic cluster complex [Ru₃(μ-H)(μ-CO)(CO)₁₀]⁻ reacts with 3,5-dimethylpyrazole (Hdmpz) to give [Ru₃(μ-dmpz)(μ-CO)₁₀(CO)]⁻ (1) in high yield. The reactivity of complex 1 with protic acids, alkynes, tertiary silanes, and tertiary stannanes is described. Complex 1 reacts with trifluoroacetic acid to give the known neutral hydrido derivative [Ru₃(μ-H)(μ-dmpz)(CO)₁₀] (2). With diphenylacetylene, complex 1 gives [Ru₃(μ-dmpz)(μ₃-PPh₂C₆H₄)(μ-CO)₁₀(CO)]⁻ (3), in which the alkynyl ligand interacts with the three ruthenium atoms. An X-ray structure analysis of [PPN]₃ is reported. Complex 2 reacts with 2 equiv of tertiary silanes or stannanes to give [Ru₃(μ-dmpz)(μ-H)(μ)(ER₂)(μ-CO)₁₀(CO)]⁻ (ER₂ = SiEt₃ (4), SiOMe₂ (5), SiPh₃ (6), SnBu₃ (7), SnPh₃ (8)). Their spectroscopic data (IR, ¹H and ¹³C NMR) indicate that the structure of the dihydrodisilyl complexes 4-6 (C₁ symmetry) is different from that of the dihydrodistannyl derivatives 7 and 8 (C₂ symmetry). Compound 1 does not promote the hydrosilation of alkynes; in fact, the reaction of complex 3 with tertiary silanes affords cis- and trans-stilbene as the only alkynyl-derived products, and complexes 4-8 do not react with phenyl- or diphenylacetylene. All anionic cluster complexes have been prepared as [Et₃N]⁻ and [PPN]⁺ salts.

Introduction

Most of the reactions of organosilanes with unsaturated organic substrates are catalyzed by transition-metal compounds. These reactions have become important in organic synthesis, and some of them are of interest in connection with industrial processes. In the case of ruthenium carbonyl cluster complexes, [Ru₃(CO)₁₂] has been demonstrated to be an efficient catalyst precursor for alkene hydrosilylation and for the synthesis of vinylsilanes from alkenes. The anionic cluster [Ru₃(μ-H)(μ-CO)(CO)₁₀]⁻ has been found to promote the reaction of ethylene with CO and HSiEt₃ to give unsaturated silyl ethers, the coupling of silanes with CO₂ to give silyl formates, and the spirocyclization of isocyanates in the presence of HSiEt₃. It has also been reported that a mixture of [Ru₃(μ-H)(μ₃-NPhpy)-]

(CO)₉ (HNPhpy = 2-anilinopyridine) and HSiEt₃ promotes the polymerization of phenylacetylene. However, in contrast with this interesting catalytic activity, very little is known about the mechanisms governing these reactions and very few papers dealing with the reactivity of ruthenium carbonyl cluster complexes with organosilanes have been published.

It is known that tertiary silanes react with [Ru₃(μ-H)(μ-CO)(CO)₁₀] to give mono-, bi-, and trinuclear derivatives. Analogous reactions with [Ru₃(μ-H)(μ-CO)(CO)₁₀] only give trinuclear products. Recently, we have described the reactivity of tertiary silanes with [Ru₃(μ-H)(μ₃-ampy)(CO)₉] (Hampy = 2-amino-6-methylpyridine), [Ru₃(μ-pyzd)(μ-CO)(CO)₉] (pyzd = pyrazidine), and [Ru₃(μ-NO)(CO)₉] in which the alkyne-derived products, and complexes 4-8 do not react with phenyl- or diphenylacetylene. All anionic cluster complexes have been prepared as [Et₃N]⁻ and [PPN]⁺ salts.

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it seems clear that the presence of bridging ligands is important in order to maintain the cluster nuclearity.

Although the reactions of tertiary stannanes with unsaturated organic molecules usually are not metal-catalyzed,
the reactivity of mononuclear transition-metal complexes with tertiary silanes and stannanes can be compared in many respects.
However, we still know very little about the reactivity of metal cluster complexes with these two reagents,
therefore, more reactivity studies of metal clusters with silanes and stannanes are needed in order to rationalize their behavior.

This article reports the synthesis of a new anionic ruthenium carbonyl cluster, [Ru₃(μ-dmpz)(μ-CO)₁₀]⁻ (1; dmpz = 3,5-dimethylpyrazole), its reactions with protic acids, alkynes, silanes, and stannanes, and some attempts to hydrosilylate alkynes using complex 1 as catalyst precursor. We initially used HSiEt₃, HSi(OMe)₃, and HSnBu₃ as reagents, but since their products were oils which proved to be very difficult to crystallize, we also carried out the reactions using HSiPh₃ and HSnPh₃. We chose complex 1 as starting material because anionic compounds are more prone to undergo oxidative addition reactions than their neutral precursors and because N-donor ligands are good cis-labilizers, facilitating the substitution of CO ligands.

Furthermore, the methyl groups on the pyrazolyl ligand help to monitor the reactions by NMR spectroscopy. Only a few trinuclear pyrazolyl derivatives of ruthenium carbonyl have been reported to date. They are the neutral compounds [Ru₃(μ-H)(μ-3,5-R₂C₂HN₂)(CO)₁₀] (R = H, Me, CF₃).

**Results and Discussion**

The cluster anion [Ru₃(μ-dmpz)(μ-CO)₁₀]⁻ (1) has been prepared in good yield (65–85%), as the [Et₄N]⁺ or [PPN]⁺ salt, by treating [Ru₃(μ-H)(μ-CO)₁₀]⁻ with 3,5-dimethylpyrazole in THF at reflux temperature (Scheme 1). The cluster contains terminal and bridging CO ligands (IR) and has a symmetric structure (GI, as indicated by its 'H and 13C NMR spectra, which confirm the presence of a symmetry plane perpendicular to the pyrazolyl ring. The structure proposed in Scheme 1 is also based on that reported for the related anionic triruthenium carbonyl cluster [Ru₃(μ-Opy)(μ-CO)₁₀]⁻ (HOpy = 2-pyridone), which has been characterized by X-ray diffraction methods. Very few anionic ruthenium cluster complexes containing N-donor heterocycles have been reported to date.

The efficient preparation of anion 1, described above, allowed a study of its reactivity. In order to confirm that 1 is a decacarbonyl derivative, its reaction with protic acids was studied. This was expected to lead to the known, neutral hydrido derivative [Ru₃(μ-H)(μ-dmpz)(CO)₁₀] (2; Scheme 2). Effectively, the reaction of complex 1 with trifluoroacetic acid gives complex 2 in excellent yield (80%, based on initial [Ru₃(CO)₁₂]). Analogous results are obtained when HBF₄·OEt₂ is substituted for trifluoroacetic acid. It is interesting to note that, under thermal conditions, the reaction of [Ru₃(CO)₁₂] with 3,5-dimethylpyrazole, in a 1:1 mole ratio, only affords small amounts (<20%) of complex 1, whereas the use of an excess of pyrazole ligand leads to the binuclear derivative [Ru₂(μ-dmpz)(μ-CO)]⁺ (20–22) based on initial [Ru₃(CO)₁₂]. The synthetic strategy consisting of (a) transformation of [Ru₃(CO)₁₂] into [Ru₃(μ-H)(μ-CO)₁₀]⁻, (b) reaction of [Ru₃(μ-H)(μ-CO)₁₀]⁻ with a protic N-donor ligand, and (c) protonation of the resulting anionic complex has been used before to prepare neutral hydridocarbonyl-triruthenium clusters containing N-donor ligands which are not conveniently made by direct reaction of [Ru₃(CO)₁₂] with the appropriate ligand.

The thermal reaction of complex 1 with phenylacetylene (1:1 mole ratio, THF, reflux temperature, 30 min) gives a mixture of at least three compounds (NMR evidence) which we could not separate and identify. However, a similar reaction with diphenylacetylene renders the anionic alkyne derivative [Ru₃(μ-dmpz)](μ₄-Ph₂C)₂(μ-CO)₁₀]⁻ (3) in quantitative spectroscopic yield (Scheme 3). Its IR spectrum shows terminal and bridging CO ligands, and its 1H and 13C NMR spectra are consistent with a structure in which a symmetry

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19) For a review on ruthenium clusters containing N-donor ligands, see: Bruce, M. I.; Gifuentes, M. P.; Humphrey, M. G. Polyhedron 1991, 10, 277.
X-ray diffraction study of the [PPNl+ salt was carried out. Table 1. The anion consists of an isosceles triangle of ruthenium atoms in which one Ru–Ru distance, Ru(1)–Ru(2), is ca. 0.1 Å longer than the other two. The dpmpz ligand spans the longest Ru–Ru edge, forming a dihedral angle of 150.5(1)° with the Ru3 plane. The structural features of this ligand are comparable to those previously observed in binuclear ruthenium carbonyl complexes.20–22 The alkyn ligand is placed on the same Ru3 face as the pyrazolyl ligand, interacting with the three ruthenium atoms in such a way that the C(14)–C(21) vector is parallel to the Ru(1)–Ru(3) edge. The Ru(1)–C(14) and Ru(3)–C(21) distances are ca. 0.1 Å shorter than the Ru(2)–C(14) and Ru(2)–C(21) distances. The alkyn C(14)–C(21) bond distance (1.371(6) Å) indicates a reduction of the C–C bond order upon coordination and correlates well with the C(14)–C(21)–C(22) and C(15)–C(14)–C(21) bond angles (125.5(4)° and 126.9(4)°, respectively).23 The cluster shell is completed by six terminal CO ligands and two semibridging CO ligands. The latter span the shorter Ru–Ru edges, being closer to Ru(1) and Ru(3) than to Ru(2). Although many carbonyl metal clusters containing alkyne ligands have been reported,23–25 to our knowledge, only two anionic derivatives of ruthenium have been structurally characterized, namely, [PPN[Ru3(μ-CH=CH2)(µ-CH2=CH2)CO]3] and [PPN[Ru3(μ-Cl)(µ-CH=CH2)(µ-CH2=CH2)CO]3].26 In these two compounds, the alkyn ligands are coordinated to the three metal atoms and are parallel to a Ru–Ru edge, as occurs in complex 3; however, although the chloride and pyrazolyl ligands behave as 3-electron donors in their respective complexes, the chloro complex [Ru3(μ-Cl)(µ-CH=CH2)(µ-CH2=CH2)CO]3 is an open 50-electron cluster, whereas complex 3 is a closed 48-electron species.

The reactions of complex 1 with tertiary silanes and stannanes (THF, reflux temperature) lead to the disilyle [Scheme 4] or distannyl (Scheme 5) dihydroxy derivatives [Ru3(μ-dmpz)(µ-CH2)(µ-CHO)3] (ERz = SiEt3 (4), Si(Me)2Ph (5), SiPh3 (6), SnBu3 (7), SnPh3 (8)). IR monitoring of the reactions indicated that at least 2 equiv of silane or stannane is needed to consume all complex 1. No reaction intermediates can be detected by spectroscopic means (IR). A similar situation has been observed before for the clusters [Ru3(μ-H)(µ-CO)(µ-H)3(CO)10] and [Ru3(μ-pydz)(µ-CO)(µ-H)3(CO)11],12 which also take 2 equiv of silanes or stannanes. However, only 1 equiv of these reagents can be incorporated into the cluster shell by spectroscopic means (IR).

Figure 1 shows the structure of anion 3 in [PPNl3. A selection of bond distances and angles is given in Table 1. The anion consists of an isosceles triangle of ruthenium atoms in which one Ru–Ru distance, Ru(1)–Ru(3), is ca. 0.1 Å longer than the other two. The dpmpz ligand spans the longest Ru–Ru edge, forming a dihedral angle of 150.5(1)° with the Ru3 plane. The structural features of this ligand are comparable to those previously observed in binuclear ruthenium carbonyl complexes.20–22 The alkyn ligand is placed on the same Ru3 face as the pyrazolyl ligand, interacting with the three ruthenium atoms in such a way that the C(14)–C(21) vector is parallel to the Ru(1)–Ru(3) edge. The Ru(1)–C(14) and Ru(3)–C(21) distances are ca. 0.16 Å shorter than the Ru(2)–C(14) and Ru(2)–C(21) distances. The alkyn C(14)–C(21) bond distance (1.371(6) Å) indicates a reduction of the C–C bond order upon coordination and correlates well with the C(14)–C(21)–C(22) and C(15)–C(14)–C(21) bond angles (125.5(4)° and 126.9(4)°, respectively).23 The cluster shell is completed by six terminal CO ligands and two semibridging CO ligands. The latter span the shorter Ru–Ru edges, being closer to Ru(1) and Ru(3) than to Ru(2). Although many carbonyl metal clusters containing alkyne ligands have been reported,23–25 to our knowledge, only two anionic derivatives of ruthenium have been structurally characterized, namely, [PPN[Ru3(μ-CH=CH2)(µ-CH2=CH2)CO]3] and [PPN[Ru3(μ-Cl)(µ-CH=CH2)(µ-CH2=CH2)CO]3].26 In these two compounds, the alkyn ligands are coordinated to the three metal atoms and are parallel to a Ru–Ru edge, as occurs in complex 3; however, although the chloride and pyrazolyl ligands behave as 3-electron donors in their respective complexes, the chloro complex [Ru3(μ-Cl)(µ-CH=CH2)(µ-CH2=CH2)CO]3 is an open 50-electron cluster, whereas complex 3 is a closed 48-electron species.

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Table 1. Selected Bond Lengths and Bond Angles in [PPNl3

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)–Ru(2)</td>
<td>Ru(1)–C(1)–C(3)</td>
</tr>
<tr>
<td>2.759(1)</td>
<td>146.6(5)</td>
</tr>
<tr>
<td>Ru(2)–Ru(3)</td>
<td>Ru(2)–C(6)–0(6)</td>
</tr>
<tr>
<td>2.769(1)</td>
<td>125.6(5)</td>
</tr>
<tr>
<td>Ru(3)–N(2)</td>
<td>Ru(3)–C(21)–Ru(3)</td>
</tr>
<tr>
<td>2.135(4)</td>
<td>124.9(2)</td>
</tr>
<tr>
<td>Ru(1)–C(3)–0(3)</td>
<td>Ru(1)–C(3)–0(3)</td>
</tr>
<tr>
<td>1.939(6)</td>
<td>126.6(5)</td>
</tr>
<tr>
<td>Ru(2)–C(6)–0(6)</td>
<td>Ru(2)–C(6)–0(6)</td>
</tr>
<tr>
<td>1.942(6)</td>
<td>126.6(5)</td>
</tr>
<tr>
<td>Ru(3)–C(21)–Ru(3)</td>
<td>Ru(3)–C(21)–Ru(3)</td>
</tr>
<tr>
<td>1.931(6)</td>
<td>126.6(5)</td>
</tr>
<tr>
<td>Ru(1)–C(14)–Ru(2)</td>
<td>Ru(1)–C(14)–Ru(2)</td>
</tr>
<tr>
<td>1.371(4)</td>
<td>126.6(5)</td>
</tr>
<tr>
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<tr>
<td>C(15)–C(14)–C(21)</td>
<td>C(15)–C(14)–C(21)</td>
</tr>
<tr>
<td>1.371(4)</td>
<td>126.6(5)</td>
</tr>
</tbody>
</table>

23 A correlation between the RC–CR distances and the C–C–R distances for a large number of complexes containing alkynes as ligands has been reported: Gervasio, G.; Rossetti, R.; Stangellini, P. L. Organometallics 1985, 4, 1612.
clusters [Ru$_3$(CO)$_{11}$(MeCN)$_2$]$^{26}$ and [Ru$_3$(μ-H)(μ$_3$-ampy)-
(CO)$_9$]$^{12,27}$ whereas in similar reactions with [Ru$_3$(μ-
NO)(CO)$_{10}$]$^-$, mono- and diisyl or distannyl derivatives
can be obtained depending on the reaction conditions.$^{13}$

The IR spectra of the silyl derivatives 4–6 are different
from those of the stannyl complexes 7 and 8. This
suggests different structures. The $^1$H NMR spectra of the
silyl derivatives show two hydride and two methyl
resonances, whereas those of the stannyl complexes only
show one hydride$^{28}$ and one methyl resonance, indicating
that the silyl derivatives are asymmetric ($C_1$) and
that the stannyl derivatives are symmetric ($C_2$).
This structural difference was confirmed by the $^{13}$C NMR
spectra of these compounds, which, apart from the
resonances of the organic fragments (that also reflect
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spectra of these compounds, which, apart from the
resonances of the organic fragments (that also reflect
complexes depicted in Schemes 4 and 5 for these compounds are consistent with their spectroscopic data,
but unfortunately, they could not be confirmed by X-ray
diffraction studies since the compounds could not be
obtained as single crystals.$^{29}$

To date, apart from the examples described in this
article, only one ruthenium cluster, [Ru$_3$(μ-pyzd)$(μ$-CO)$_2$-
(CO)$_2$]$^-$, is known to behave in a way similar to that for
complex 1, giving asymmetric disilyl and symmetric
distannyl derivatives.$^{12}$ The disilyl and distannyl de-
rivatives of [Ru$_3$(μ-H)(μ$_3$-CO)(CO)$_2$]$^-$ are isosctructural.
$^{10,30}$ whereas [Ru$_3$(μ-NO)(CO)$_{10}$]$^-$ gives symmetric
disilyl and asymmetric distannyl products.$^{13}$ Interest-
ingly, the cluster complexes which only add 1 equiv of
HSiR$_3$ or HSnR$_3$ give isostructural produ~ts.$^{28,29,30}$ This
particular behavior of tertiary silanes and stannanes in
their reactions with carbonyl cluster compounds is
intriguing, and its explanation needs much more work
in this area.

As the preparation of vinylsilanes is currently of great
interest,$^{1,31}$ we investigated the reactivity of the alkyn
complex 3 with tertiary silanes, the reactivity of the silyl
dervatives 4 and 5 with alkynes, and the activity of
complex 1 as a catalyst precursor for the synthesis of
vinylsilanes via hydrosilylation of alkynes.

The reaction of complex 3 with tertiary silanes (1,2-
dichloroethane, reflux temperature) gives cis- and trans-
stibene, as the only alkyn-derived products, and an
inseparable mixture of cluster compounds. A similar
reaction with HSnPh$_3$ (1,2-dichloroethane, room
temperature) gives diphenylacetylene and the distannyl
complex 8. On the other hand, no reaction was observed
between complexes 4–8 and phenyl- or diphenylacety-
lene. These results are in accordance with the fact that
no vinylsilanes are produced when complex 1, HSiEt$_3$
and phenyl- or diphenylacetylene are allowed to react
in 1,2-dichloroethane under catalytic conditions (1:80:
50 mole ratio, 80 °C, 1 h).

In conclusion, this paper reports an efficient synthesis
of complex 1, a novel anionic ruthenium carbonyl cluster
containing a bridging N-donor heterocyclic ligand (a
thus far uncommon class of compound), and its reactivity
with alkynes, tertiary silanes, and tertiary stannanes.
The X-ray-characterized alkyn complex 3 adds a
new example to the very few in which the coordination
of alkynes to anionic clusters has been reported.
Finally, the results of the reactivity studies of complex 1
with tertiary silanes and stannanes, although are far
from being explainable, may contribute to shed light on
the behavior of these reagents in their reactions with
carbonyl cluster complexes.

### Experimental Section

**General Data.** Solvents were dried over sodium diphenyl
ketal, THF, diethyl ether, hydrocarbons, magnesium (methyl-
ol), or CaH$_2$ (dichloromethane, 1,2-dichloroethane) and dis-
tilled under nitrogen prior to use. Unless otherwise stated,
the reactions were carried out under nitrogen at room

temperature, using Schlenk–vacuum-line techniques, and were
routine monitored by solution IR spectroscopy (carbonyl
stretching region). All reagents were used as received from
Aldrich. IR spectra were recorded in solution on a Perkin-
Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF$_2$
cells.

$^1$H and $^{13}$C NMR spectra were run at 20 °C with Bruker AC-
200 and AC-300 instruments, using SiMe$_4$ as internal standard
(s 0 ppm). Microanalyses were obtained from the University
of Oviedo Analytical Service. GC analyses were carried out
at 175 °C on a Perkin-Elmer 8600 gas chromatograph,
equipped with a 12-m Q2 capillary column and a flame
ionization detector.

The IR and NMR spectroscopic properties of the [Et$_4$N]$^+$
and [PPN]$^+$ salts of the same anionic complex are very similar;
therefore, only data corresponding to one of these salts are
given.

[Et$_4$N$^+$][Ru$_3$(μ-dmpz)(μ$_2$-CO)(CO)$_3$]$^-$ ([Et$_4$N]$^+$]
A solution of [Ru$_3$(CO)$_{12}$(CO)$_{12}$(MeCN)$_2$]$^-$ (35 mg, 0.938 mmol) in methanol
(5 mL) was added to a solution of [Ru$_3$(CO)$_{12}$(CO)$_{12}$] (400 mg, 0.625 mmol) in warm THF
(40 mL, 40 °C). The color changed from orange to deep red.
The solvent was evaporated under reduced pressure and the residue
redissolved in THF (30 mL). At this point, an IR
spectrum of the solution indicated only the presence of Na-
[Ru$_3$(CO)$_{12}$(CO)$_{12}$]$^-$ (addition of Hmpz (90 mg, 0.938 mmol), the solution was stirred at reflux temperature for 1.5
h. A solution of [Et$_4$N]Br (144 mg, 0.688 mmol) in methanol
(5 mL) was added. The solvent was evaporated under reduced pressure
and the residue extracted into dichloromethane (40 mL)
to remove insoluble NaBr. The filtered solution was
evaporated to dryness and the residue washed with hexane
(3 × 3 mL) to give [Et$_4$N]$^+$ as a yellow solid (417 mg, 83%).
Anal. Calc. for $C_{57}H_{57}N_9O_{10}Ru_3$: C, 34.16; H, 3.36; N, 5.20.

Found: C, 34.61; H, 3.40; N, 5.00. IR ν(CO) (THF): 2071 (w),
2015 (vs), 1985 (vs), 1950 (m), 1852 (s), 1807 (s), 1800 (s) cm$^{-1}$.
$^1$H NMR (CD$_2$Cl$_2$): 5.23 (s, 1H), 1.79 (s, 6H)
dmpz ppm; 5.17 (q, 8 H), 1.31 (s, 12 H) [Et$_4$N$^+$] ppm.
$^{13}$C[($^1$H)] NMR (CD$_2$Cl$_2$): 227.1, 205.6, 202.0 (CO) ppm;
149.7, 106.8, 13.8 (dmpz) ppm; 54.2, 8.9 (Et$_4$N) ppm.

A solution of [PPN]$^+$ (380 mg, 0.687 mmol) in dichloromethane
(40 mL) was added to a solution of [Ru$_3$(CO)$_{12}$(CO)$_{12}$] (400 mg, 0.625
mmol) in THF (40 mL). The color changed from orange to deep red.
After the mixture was stirred for 15 min, the solvent was evaporated under reduced pressure and the residue
redissolved in THF (20 mL). At this point, an IR spectrum of the solution
indicated only the presence of [PPN$^+$][Ru$_3$(μ$_2$-CO)(CO)$_3$]$^-$.

After addition of Hmpz (66 mg, 0.687 mmol), the solution was
stirred at reflux temperature for 2 h. The solvent was removed
under reduced pressure and the residue washed with hexane (3 × 4 mL) to give [PPN]1 as a yellow solid (490 mg, 64%).

Anal. Calcd for C53H59NO3P2Ru2: C, 53.8; H, 4.9; N, 3.1. Found: C, 53.8; H, 4.9; N, 3.1.

[Ru2(μ-H)(μ-dmpz)(CO)2(C≡N)](2). Trifluoroacetic acid (1 mL) was added to a solution of Na[Ru(μ-H)(μ-dmpz)(CO)2(C≡N)](prepared in situ, as described above, from [Ru2(CO)2] (1 g, 1.564 mmol), Na[BH4] (89 mg, 2.35 mmol), and Hدمز (225 mg, 2.35 mmol) in dichloromethane (15 mL). The mixture was stirred for 25 min and evaporated to dryness. The residue was then extracted into dichloromethane (3 mL) and filtered through a short (5 × 2 cm) column of neutral alumina (activity 1). The column was washed with dichloromethane and the resulting solution evaporated to dryness to give an oil which was redissolved in pentane. The solution was then evaporated to give complex 2 as an orange solid (850 mg, 80%).

Anal. Calcd for C53H59NO3P2Ru2: C, 56.5; H, 3.5; N, 3.1. Found: C, 56.9; H, 3.5; N, 3.1.

Selected 13C{1H} NMR (CD2Cl2): 202.9, 199.3, 199.2, 197.9, 197.1, 196.2, 190.6, 182.1 (CO) ppm; 181.3, 180.6 (Ph2C2), 156.2 (ipso-C of Ph2C2) ppm; 147.8, 147.2, 107.3, 106.3, 12.6 (dmpz) ppm.

1H NMR (CD2Cl2): 5.46 (s, 6 H), 1.95 (s, 3 H) (dmpz) ppm; 2.12 (s, 6 H) (dmpz) ppm; 3.13 (q, 8 H), 1.18 (t, 12 H) (EtN) ppm; 0.95 (m, 30 H, SiEt3) ppm; -11.17 (d, J = 2 Hz, 1 H) (μ-H) ppm.

The compound [PPN]3 was prepared in a similar way (71% yield), with [PPN]1 as starting material. Anal. Calcd for C53H59NO3P2Ru2Si2: C, 60.7; H, 4.1; N, 2.50. Found: C, 61.0; H, 4.1; N, 2.70.

[PPN][Ru(μ-dmpz)(μ-H)2(Si(OMe)3)2(CO)] (IPPn)6). A solution of [PPN]1 (70 mg, 0.087 mmol) and HSi(OMe)3 (20 mL, 0.155 mmol) in THF (10 mL) was stirred at reflux temperature for 2 h. The color changed from yellow to orange. The solution was evaporated to dryness and the residue washed with hexane (2 × 4 mL) to give [IPPn]6 as an orange air-sensitive oil which could not be crystallized. IR ν(CO) (THF): 2066 (w), 2030 (vs), 1991 (sh), 1972 (sh) cm⁻¹. 1H NMR (CD2Cl2): 134.1, 51.2, 47.4, 43.8, 33.5, 30.4, 29.2, 28.4 (MeO) ppm.

The compound [IPPn]7 (violet oil) was prepared in a similar way (71% yield), with [IPPn]1 as starting material. Anal. Calcd for C53H59NO3P2Ru2Si2: C, 60.7; H, 4.1; N, 2.50. Found: C, 61.0; H, 4.1; N, 2.70.
Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å² × 10^3) for the Non-H Atoms of [PPN]Cl

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<th>y/b</th>
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* U_eq is defined as one-third of the trace of the orthogonalized U_eq tensor.

**H**^{(1)}Et_4N ppm: -10.33 (s with satellites, J = 30 Hz, 2 H, H, H) ppm. Selected 2HCH NMR (CD_2Cl_2): 205.8, 199.9, 199.5, 199.3, 198.9 (CO) ppm: 146.9, 106.9, 13.6 (dmppz ppm: 54.6, 7.7, 7.7 ppm).

The compound [PPN]Cl was prepared in a similar way (66% yield), with [PPN]Cl as starting material. Calcd for C_6H_10O_2N_4Et_4C_6H_4N_3: C, 54.80; H, 3.73; N, 2.25. Found: C, 55.08; H, 3.80; N, 3.90.

**Reaction of [NETu]Cl with HSiPh_3.** A solution of [NETu]Cl (50 mg, 0.0053 mmol) and HSiPh_3 (38 mg, 0.107 mmol) in 1,2-dichloroethane (10 mL) was stirred for 20 min at room temperature. As no reaction was observed, the solution was then heated at reflux temperature for 20 min. The color changed from red to orange. The solution was evaporated to dryness and the residue washed with diethyl ether. A H NMR spectrum of the solid revealed a mixture of complexes in which [EtN]Cl was the major component. A GC analysis of the etherial solution indicated the presence of cis- and trans-stilbene. Analogous results were obtained when HSiEt_3 was substituted for HSiPh_3.

**Reaction of [NETu]Cl with HSnPh_3.** A solution of [NETu]Cl (100 mg, 0.107 mmol) and HSnPh_3 (86 mg, 0.247 mmol) in 1,2-dichloroethane (10 mL) was stirred for 20 min. The color changed from red to violet. The solution was evaporated to dryness and the residue washed with diethyl ether. A H NMR spectrum of the solid revealed the presence of [EtN]Cl. A GC analysis of the etherial solution indicated the presence of diphenylsilane.

**Crystall Structure of [PPN]Cl.** A dark red crystal, obtained by layering pentane on a solution of the complex in diethyl ether at -20 °C, was used for the X-ray diffraction study. A selection of crystal and refinement data is given in Table 2.

The cell dimensions were determined by least-squares refinement of 25 reflections with 15 < θ < 20°. The space group P2_1 was found from systematic absences. Intensities were collected with a variable scan rate and a maximum scan time of 60 s per reflection. Three standard reflections were monitored every 60 min, revealing no intensity fluctuations. Final drift correction factors were between 0.98 and 1.03. Profile analysis was performed on all reflections. An empirical absorption correction based on θ-scans was applied. An empirical absorption correction based on θ-scans was applied. An empirical absorption correction based on θ-scans was applied. An empirical absorption correction based on θ-scans was applied.

The structure was solved by Patterson interpretation using DIRDIF92. An isotropic least-squares refinement, using a local version of SHELX, was followed by a semiempirical absorption correction based on θ-scans.

School of Chemistry, University of Oviedo, Oviedo, Spain, 1991.


tion correction (minimum, maximum correction factors 0.28, 0.34). Full-matrix anisotropic least-squares refinement over \( F^2 \), using the program SHELXL93, followed by a difference Fourier synthesis allowed the location of all the hydrogen atoms. After refinement of the positional and anisotropic thermal parameters of the non-hydrogen atoms, the hydrogen atoms were refined isotropically, using a riding model, with free distances to the parent atoms and free rotation for the methyl groups. The thermal parameter used for the hydrogens of the methyl groups was different from that used for the remaining hydrogen atoms. The function minimized was 
\[
\sum w(F_i^2 - F_o^2)^2, \quad w = 1/(\sigma^2(F_i^2) + (0.0368P^2 + 0.5332P),
\]
with \( \sigma(F_o) \) from counting statistics and \( P = (F_o^2 - 2F_i^2)/3 \). Atomic scattering factors were taken from ref 39. Geometrical calculations were made with PARST. The structure plot was drawn with the EUCLID package. Final atomic coordinates are given in Table 3. All calculations were carried out on a MicroVax3400 computer at the Scientific Computer Center of the University of Oviedo.

**Acknowledgment.** This research was supported by the DGICYT (Spain, Grant PB92-1007). R.J.F. is grateful to MUTIS and the Instituto de Cooperación Iberoamericana for postgraduate scholarships.

**Supporting Information Available:** Tables of bond distances and angles, anisotropic thermal parameters, and H-atom coordinates for \([\text{PPN}]_3\) (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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