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

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The anionic cluster complex $[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$ reacts with 3,5-dimethylpyrazole (Hdmpz) to give $[Ru_3(\mu\text{-dmpz})(\mu\text{-CO})_3(CO)_7]^-$ (**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 $[Ru_3(\mu\text{-H})(\mu\text{-dmpz})(CO)_{10}]$ (**2**). With diphenylacetylene, complex **1** gives $[Ru_3(\mu\text{-dmpz})(\mu_3\text{-}Ph_2C_2)(\mu\text{-CO})_2(CO)_6]^-$ (**3**), in which the alkyne 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 $[Ru_3(\mu\text{-dmpz})(\mu\text{-H})_2(ER_3)_2(CO)_8]^-$ (ER_3 = $SiEt_3$ (**4**), $Si(OMe)_3$ (**5**), $SiPh_3$ (**6**), $SnBu_3$ (**7**), $SnPh_3$ (**8**)). Their spectroscopic data (IR, ^1H and ^{13}C NMR) indicate that the structure of the dihydrido disilyl complexes **4**–**6** (C_1 symmetry) is different from that of the dihydrido distannyl derivatives **7** and **8** (C_s symmetry). Compound **1** does not promote the hydrosilylation of alkynes; in fact, the reaction of complex **3** with tertiary silanes affords *cis*- and *trans*-stilbene as the only alkyne-derived products, and complexes **4**–**8** do not react with phenyl- or diphenylacetylene. All anionic cluster complexes have been prepared as $[Et_4N]^+$ 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,[1] and some of them are of interest in connection with industrial processes.[1,2]

In the case of ruthenium carbonyl cluster complexes, $[Ru_3(CO)_{12}]$ has been demonstrated to be an efficient catalyst precursor for alkene hydrosilylation[3] and for the synthesis of vinylsilanes from alkenes.[4] The anionic cluster $[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$ has been found to promote the reaction of ethylene with CO and $HSiEt_3$ to give unsaturated silyl ethers,[5] the coupling of silanes with CO_2 to give silyl formates,[6] and the spirocyclization of isocyanates in the presence of $HSiEt_3$.[7] It has also been reported that a mixture of $[Ru_3(\mu\text{-H})(\mu_3\text{-NPhpy})(CO)_9]$ (HNPhpy = 2-anilinopyridine) and $HSiEt_3$ promotes the polymerization of phenylacetylene.[8] 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.[9–13]

It is known that tertiary silanes react with $[Ru_3(CO)_{12}]$ to give mono-, bi-, and trinuclear derivatives.[9] Analogous reactions with $[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$ only give trinuclear products.[10] Recently, we have described the reactivity of tertiary silanes with $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (Hampy = 2-amino-6-methylpyridine),[11] $[Ru_3(\mu\text{-pydz})(\mu\text{-CO})_3(CO)_7]$ (pydz = pyridazine),[12] and $[Ru_3(\mu\text{-NO})(CO)_{10}]^-$;[13] in these three cases, the products are also trinuclear derivatives. From these examples,

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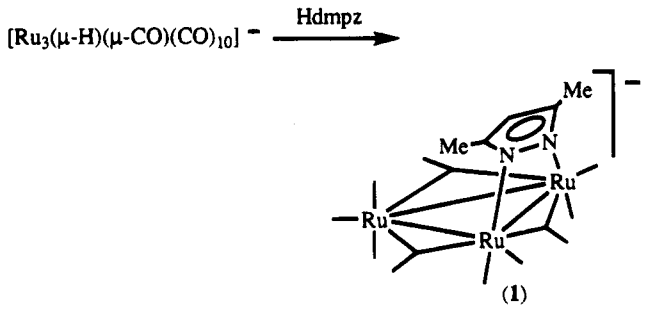
Scheme 1



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,[14] the reactivity of mononuclear transition-metal complexes with tertiary silanes and stannanes can be compared in many respects.[15,16] However, we still know very little about the reactivity of metal cluster complexes with these two reagents;[15,16] therefore, more reactivity studies of metal clusters with silanes and stannanes are needed in order to rationalize their behavior.

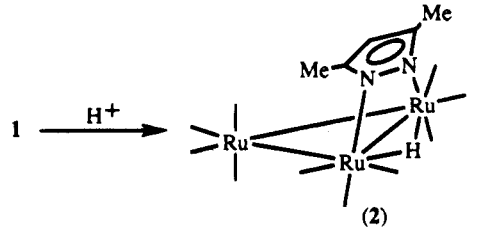
This article reports the synthesis of a new anionic ruthenium carbonyl cluster, $[Ru_3(\mu\text{-dmpz})(\mu\text{-CO})_3(CO)_7]^-$ (**1**; Hdmpz = 3,5-dimethylpyrazole), its reactions with protic acids, alkynes, silanes, and stannanes, and some attempts to hydrosilylate alkynes using complex **1** as catalyst precursor. We initially used $HSiEt_3$, $HSi(OMe)_3$, and $HSnBu_3$ as reagents, but since their products were oils which proved to be very difficult to crystallize, we also carried out the reactions using $HSiPh_3$ and $HSnPh_3$. 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.[11-13] 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 $[Ru_3(\mu\text{-H})(\mu\text{-3,5-}R_2C_3HN_2)(CO)_{10}]$ (R = H, Me, CF_3).[17]

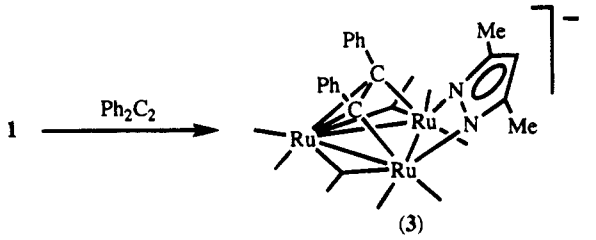
Results and Discussion

The cluster anion $[Ru_3(\mu\text{-dmpz})(\mu\text{-CO})_3(CO)_7]^-$ (**1**) has been prepared in good yield (65–85%), as the $[Et_4N]^+$ or $[PPN]^+$ salt, by treating $[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$ 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 (C_s), as indicated by its ^1H and ^{13}C 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 $[Ru_3(\mu\text{-Opy})(\mu\text{-CO})_3(CO)_7]^-$ (HOpy = 2-pyridone), which has been characterized by

Scheme 2



Scheme 3



X-ray diffraction methods.[18] Very few anionic ruthenium cluster complexes containing N-donor heterocycles have been reported to date.[18,19]

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,[17] neutral hydrido derivative $[Ru_3(\mu\text{-H})(\mu\text{-dmpz})(CO)_{10}]$ (**2**; Scheme 2). Effectively, the reaction of complex **1** with trifluoroacetic acid gives complex **2** in excellent yield (80%, based on initial $[Ru_3(CO)_{12}]$). Analogous results are obtained when $HBF_4{\cdot}OEt_2$ is substituted for trifluoroacetic acid. It is interesting to note that, under thermal conditions, the reaction of $[Ru_3(CO)_{12}]$ with 3,5-dimethylpyrazole, in a 1:1 mole ratio, only affords small amounts (<20%) of complex **2**,[17,20] whereas the use of an excess of pyrazole ligand leads to the binuclear derivative $[Ru_2(\mu\text{-dmpz})_2(CO)_6]$.[20-22] The synthetic strategy consisting of (a) transformation of $[Ru_3(CO)_{12}]$ into $[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$, (b) reaction of $[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$ with a protic N-donor ligand, and (c) protonation of the resulting anionic complex has been used before to prepare neutral hydridocarbonyltriruthenium clusters containing bridging N-donor ligands which are not conveniently made by direct reaction of $[Ru_3(CO)_{12}]$ with the appropriate ligand.[18]

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 $[Ru_3(\mu\text{-dmpz})(\mu_3\text{-}Ph_2C_2)(\mu\text{-CO})_2(CO)_6]^-$ (**3**) in quantitative spectroscopic yield (Scheme 3). Its IR spectrum shows terminal and bridging CO ligands, and its ^1H and ^{13}C NMR spectra are consistent with a structure in which a symmetry

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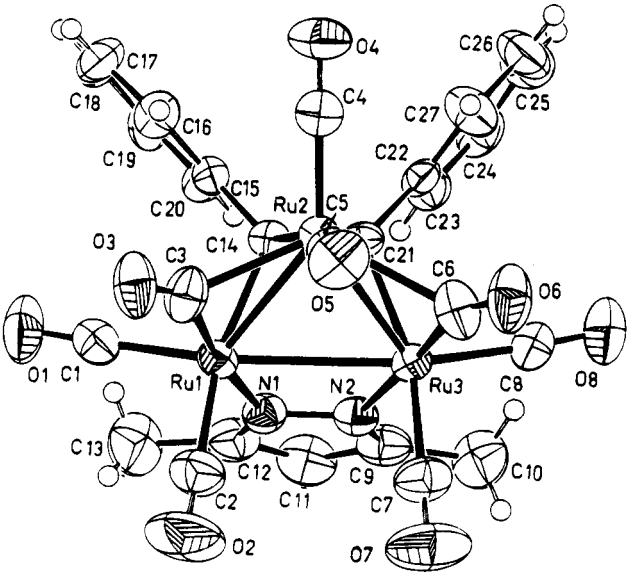


Figure 1. EUCLID structural plot of the anion $[Ru_3(\mu\text{-dmpz})(\mu_3\text{-}Ph_2C_2)(\mu\text{-}CO)_2(CO)_6]^-$ (**3**) in [PPN]**3**. Thermal ellipsoids are drawn at the 50% probability level.

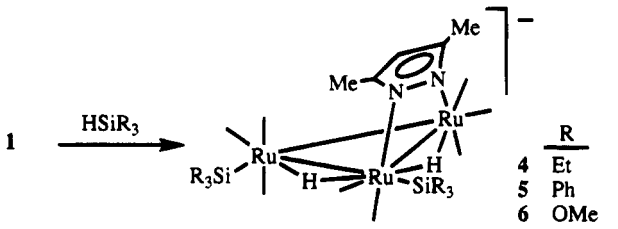
Table 1. Selected Bond Lengths and Bond Angles in [PPN]3

Bond Lengths (Å)			
Ru(1)–Ru(2)	2.753(1)	Ru(1)–Ru(3)	2.865(1)
Ru(2)–Ru(3)	2.769(1)	Ru(1)–N(1)	2.131(4)
Ru(3)–N(2)	2.135(4)	Ru(1)–C(1)	1.917(5)
Ru(1)–C(2)	1.939(6)	Ru(1)–C(3)	2.030(6)
Ru(1)–C(14)	2.126(4)	Ru(2)–C(3)	2.181(6)
Ru(2)–C(4)	1.864(5)	Ru(2)–C(5)	1.868(5)
Ru(2)–C(6)	2.352(6)	Ru(2)–C(14)	2.288(4)
Ru(2)–C(21)	2.286(4)	Ru(3)–C(6)	1.942(6)
Ru(3)–C(7)	1.947(5)	Ru(3)–C(8)	1.931(6)
Ru(3)–C(21)	2.133(4)	C(1)–O(1)	1.132(6)
C(2)–O(2)	1.118(7)	C(3)–O(3)	1.149(7)
C(4)–O(4)	1.141(6)	C(5)–O(5)	1.145(6)
C(6)–O(6)	1.150(6)	C(7)–O(7)	1.130(6)
C(8)–O(8)	1.26(7)	C(14)–C(21)	1.371(6)
Bond Angles (deg)			
Ru(1)–Ru(2)–Ru(3)	62.50(3)	Ru(1)–Ru(3)–Ru(2)	58.48(3)
Ru(2)–Ru(1)–Ru(3)	59.02(3)	Ru(1)–C(3)–Ru(2)	81.6(2)
Ru(1)–C(3)–O(3)	146.6(5)	Ru(2)–C(3)–O(3)	131.8(5)
Ru(2)–C(6)–Ru(3)	79.7(2)	Ru(2)–C(6)–O(6)	125.6(5)
Ru(3)–C(6)–O(6)	154.6(5)	Ru(1)–C(14)–Ru(2)	77.1(1)
Ru(2)–C(21)–Ru(3)	77.5(1)	C(14)–Ru(2)–C(21)	24.9(2)
C(15)–C(14)–C(21)	126.0(4)	C(14)–C(21)–C(22)	125.5(4)

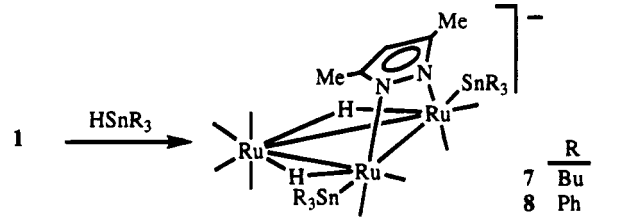
plane cuts the pyrazolyl and alkyne ligands into identical halves. As these spectroscopic data are not sufficient to unequivocally assign a structure to this cluster, an X-ray diffraction study of the $[PPN]^+$ salt was carried out.

Figure 1 shows the structure of anion **3** in [PPN]**3**. 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 dmpz ligand spans the longest Ru–Ru edge, forming a dihedral angle of 150.5(1)° with the Ru_3 plane. The structural features of this ligand are comparable to those previously observed in binuclear ruthenium carbonyl complexes.[20-22] The alkyne ligand is placed on the same Ru_3 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 alkyne 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 126.0(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 alkynes as ligands have been reported,[23-25] to our knowledge, only two anionic derivatives of ruthenium have been structurally characterized, namely, $[PPN][Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_2C_2)(CO)_9]$ and $[PPN][Ru_3(\mu\text{-}Cl)(\mu_3\text{-}Ph_2C_2)(CO)_9]$.[25] In these two compounds, the alkyne 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 $[Ru_3(\mu\text{-}Cl)(\mu_3\text{-}Ph_2C_2)(CO)_9]^-$ is an open 50-electron cluster, whereas complex **3** is a closed 48-electron species.

Scheme 4



Scheme 5



The reactions of complex **1** with tertiary silanes and stannanes (THF, reflux temperature) lead to the disilyl (Scheme 4) or distannyl (Scheme 5) dihydrido derivatives $[Ru_3(\mu\text{-dmpz})(\mu\text{-}H)_2(ER_3)_2(CO)_8]^-$ ($ER_3 = SiEt_3$ (**4**), $Si(OMe)_3$ (**5**), $SiPh_3$ (**6**), $SnBu_3$ (**7**), $SnPh_3$ (**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 $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ [10] and $[Ru_3(\mu\text{-pydz})(\mu\text{-}CO)_3(CO)_7]$,[12] which also take 2 equiv of silanes or stannanes. However, only 1 equiv of these reagents can be incorporated into the

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clusters $[Ru_3(CO)_{11}(MeCN)]$[26] and $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$,[11,27] whereas in similar reactions with $[Ru_3(\mu\text{-NO})(CO)_{10}]^-$, mono- and disilyl or distannyl derivatives can be obtained depending on the reaction conditions.[13]

The IR spectra of the silyl complexes **4**–**6** are different from those of the stannyl complexes **7** and **8**. This suggests different structures. The ^1H 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_s). 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 the symmetry of the complexes), show eight CO signals for the silyl derivatives and five CO signals for the stannyl compounds (unlike **1**–**3**, the silyl and stannyl complexes are not fluxional at room temperature). The structures 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, $[Ru_3(\mu\text{-pydz})(\mu\text{-CO})_3(CO)_7]$, is known to behave in a way similar to that for complex **1**, giving asymmetric disilyl and symmetric distannyl complexes.[12] The disilyl and distannyl derivatives of $[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$ are isostructural,[10,30] whereas $[Ru_3(\mu\text{-NO})(CO)_{10}]^-$ gives symmetric disilyl and asymmetric distannyl products.[13] Interestingly, the cluster complexes which only add 1 equiv of $HSiR_3$ or $HSnR_3$ give isostructural products.[11,13,27] 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 alkyne complex **3** with tertiary silanes, the reactivity of the silyl derivatives **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*-stilbene, as the only alkyne-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 diphenylacetylene. 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 alkyne 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 ketyl (THF, diethyl ether, hydrocarbons), magnesium (methanol), or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled 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 routinely 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. ^1H and ^{13}C NMR spectra were run at 20 °C with Bruker AC-200 and AC-300 instruments, using $SiMe_4$ as internal standard (δ 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 AQ2 capillary column and a flame ionization detector.

The IR and NMR spectroscopic properties of the $[Et_4N]^+$ and $[PPN]^+$ salts of the same anionic complex are very similar; therefore, only data corresponding to one of these salts are given.

$[Et_4N][Ru_3(\mu\text{-dmpz})(\mu\text{-CO})_3(CO)_7]$ ([Et_4N]1). A solution of $Na[BH_4]$ (35 mg, 0.938 mmol) in methanol (5 mL) was added to a solution of $[Ru_3(CO)_{12}]$ (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 $Na[Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]$. After addition of Hdmpz (90 mg, 0.938 mmol), the solution was stirred at reflux temperature for 1.5 h. A solution of $[Et_4N]Br$ (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_4N]1 as a yellow solid (417 mg, 83%). Anal. Calcd for $C_{23}H_{27}N_3O_{10}Ru_3$: 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), 1987 (vs), 1950 (m), 1935 (s), 1852 (w), 1807 (sh), 1800 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): 5.23 (s, 1H), 1.79 (s, 6H) (dmpz) ppm; 3.17 (q, 8 H), 1.31 (t, 12 H) (Et_4N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 227.1, 205.6, 202.0 (CO) ppm; 149.7, 106.8, 13.8 (dmpz) ppm; 54.2, 8.9 (Et_4N) ppm.

[PPN][$Ru_3(\mu\text{-dmpz})(\mu\text{-CO})_3(CO)_7$] ([PPN]1). A solution of [PPN][BH_4] (380 mg, 0.687 mmol) in dichloromethane (40 mL) was added to a solution of $[Ru_3(CO)_{12}]$ (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 $[PPN][Ru_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]$. After addition of Hdmpz (66 mg, 0.687 mmol), the solution was stirred at reflux temperature for 2 h. The solvent was removed

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(28) The $J(^{119/117}Sn-^1H)$ coupling constants measured in the satellites of these hydride resonances (ca. 29 Hz) are indicative of a cis arrangement of the hydride and stannyl ligands.[11-13]

(29) The structure proposed for the silyl derivatives is comparable to that of $[Ru_3(\mu\text{-pydz})(\mu\text{-H})_2(SiEt_3)_2(CO)_8]$, which has been characterized by X-ray diffraction methods.[12]

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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 $C_{51}H_{37}N_3O_{10}P_2Ru_3$: C, 50.33; H, 3.06; N, 3.45. Found: C, 49.94; H, 3.23; N, 3.31.

[$Ru_3(\mu$-H)(μ-dmpz)$(CO)_{10}$] (2). Trifluoroacetic acid (1 mL) was added to a solution of Na[$Ru_3(\mu$-dmpz)$(\mu$-$CO)_3(CO)_7$] (prepared *in situ*, as described above, from [$Ru_3(CO)_{12}$] (1 g, 1.564 mmol), Na[BH_4] (89 mg, 2.35 mmol), and Hdmpz (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 I). The column was washed with dichloromethane and the resulting solution evaporated to dryness to give an oil which was redissolved in pentane. The solvent was again evaporated to give complex **2** as an orange solid (850 mg, 80%). Anal. Calcd for $C_{15}H_8N_2O_{10}Ru_3$: C, 26.52; H, 1.19; N, 4.12. Found: C, 26.60; H, 1.18; N, 4.08. IR ν(CO) (hexane): 2105 (w), 2067 (s), 2059 (s), 2026 (vs), 2016 (w), 2008 (m), 1993 (w), 1990 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): 5.74 (s, 1 H), 2.06 (s, 6 H) (dpmz) ppm; −13.18 (s, 1 H, μ-H) ppm.

[Et_4N][$Ru_3(\mu$-dmpz)$(\mu_3$-$Ph_2C_2)(\mu$-$CO)_2(CO)_6$] ([Et_4N]3). A solution of [Et_4N]**1** (70 mg, 0.087 mmol) and diphenylacetylene (23 mg, 0.129 mmol) in THF (20 mL) was stirred at reflux temperature for 2.5 h. The color changed from yellow to orange. The solvent was removed and the residue washed with hexane (3 × 3 mL) to give [Et_4N]**3** as an orange solid (70 mg, 86%). Anal. Calcd for $C_{35}H_{37}N_3O_8Ru_3$: C, 45.16; H, 4.00; N, 4.51. Found: C, 45.29; H, 4.33; N, 4.34. IR ν(CO) (THF): 2039 (m), 1996 (vs), 1977 (s), 1969 (sh), 1935 (m), 1898 (w), 1785 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 7.6−6.6 (m, 10 H, Ph) ppm; 5.91 (s, 1 H), 2.12 (s, 6 H) (dmpz) ppm; 3.01 (q, br, 8 H), 1.18 (t, br, 12 H) (Et_4N) ppm.

The compound [PPN]**3** was prepared in a similar way (78% yield), with [PPN]**1** as starting material. Anal. Calcd for $C_{63}H_{47}N_3O_8P_2Ru_3$: C, 56.50; H, 3.54; N, 3.14. Found: C, 56.99; H, 3.71; N, 3.21. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 201.9, 193.1 (CO) ppm; 180.6 (Ph_2C_2), 156.2 (*ipso*-C of Ph_2C_2) ppm; 147.8, 106.3, 12.6 (dmpz) ppm.

[Et_4N][$Ru_3(\mu$-dmpz)$(\mu$-$H)_2(SiEt_3)_2(CO)_8$] ([Et_4N]4). A solution of [Et_4N]**1** (80 mg, 0.099 mmol) and $HSiEt_3$ (40 μL, 0.256 mmol) in THF (15 mL) was stirred at reflux temperature for 45 min. The color changed from yellow to red. The solvent was removed and the residue washed with hexane (2 × 4 mL) to give the complex [Et_4N]**4** as a red oil which could not be crystallized. IR ν(CO) (THF): 2054 (m), 2015 (m), 1999 (vs), 1969 (s), 1957 (m), 1932 (m) cm^{-1}; ^1H NMR ($CDCl_3$): 5.44 (s, 1 H), 2.00 (s, 3 H), 1.95 (s, 3 H) (dmpz) ppm; 3.12 (q, 8 H), 1.18 (t, 12 H) (Et_4N) ppm; 0.95 (m, 30 H, $SiEt_3$) ppm; −11.12 (d, J = 2 Hz, 1 H), −11.77 (d, J = 2 Hz, 1 H) (μ-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 211.7, 209.7, 208.5, 207.2, 206.6, 205.4, 199.0, 192.9 (CO) ppm; 147.8, 147.2, 104.9, 12.9, 12.8 (dmpz) ppm; 52.3, 7.2 (Et_4N) ppm; 12.4, 11.1, 9.0, 8.8 ($SiEt_3$) ppm.

The compound [PPN]**4** (red oil) was prepared in a similar way, with [PPN]**1** as starting material.

[Et_4N][$Ru_3(\mu$-dmpz)$(\mu$-$H)_2(SiPh_3)_2(CO)_8$] ([Et_4N]5). A solution of [Et_4N]**1** (80 mg, 0.099 mmol) and $HSiPh_3$ (44 mg, 0.247 mmol) in THF (20 mL) was stirred at reflux temperature for 2 h. The color changed from yellow to red. The solvent was removed and the residue extracted into diethyl ether (2 × 10 mL). The filtered solution was evaporated to dryness and the residue washed with hexane (2 × 5 mL) to give [Et_4N]-**5** as a red-orange solid (74 mg, 59%). Anal. Calcd for $C_{57}H_{59}N_3O_8Ru_3Si_2$: C, 53.76; H, 4.67; N, 3.30. Found: C, 53.98; H, 4.80; N, 3.31. IR ν(CO) (THF): 2062 (m), 2036 (sh), 2016 (s), 1983 (vs), 1971 (m), 1951 (sh), 1933 (sh) cm^{-1}. ^1H NMR ($CDCl_3$): 7.8−7.0 (m, 30 H, $SiPh_3$) ppm; 5.38 (s, 1 H), 1.95 (s, 3 H), 1.59 (s, 3 H) (dmpz) ppm; 2.97 (q, br, 8 H), 1.14 (t, br, 12 H) (Et_4N) ppm; −10.97 (s, 1 H), −11.76 (s, 1 H) (μ-H) ppm. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 202.9, 199.3, 199.2, 197.9, 197.1, 196.2, 190.6, 182.1 (CO) ppm; 146.8, 145.0, 107.3, 13.1, 12.7 (dmpz) ppm; 54.6, 7.7 (Et_4N) ppm.

Table 2. Crystallographic and Refinement Data for [PPN]3

formula	$C_{63}H_{47}N_3O_8P_2Ru_3$
fw	1339.19
cryst syst	monoclinic
space group	$P2_1$
a, b, c, Å	15.718(9), 9.580(3), 19.957(12)
β, deg	108.39(4)
V, Å^3	2852(3)
Z	2
$F(000)$	1344
D_{calcd}, g/cm^3	1.560
μ, mm^{-1}	0.899
cryst size, mm	0.36 × 0.33 × 0.13
radiation (λ, Å)	Mo Kα (0.710 73)
diffractometer	Enraf-Nonius CAD4
monochromator	graphite
temp, K	293(2)
scan method	$\omega-2\theta$
θ limits, deg	1.08−24.97
h,k,l ranges	0 to +18, o to +11, −23 to +22
no. of rflns collected	5503
no. of indep rflns	5338
$R_{int} = \sum(I - \langle I\rangle)/\sum I$	0.022
no. of rflns with $I > 2\sigma(I)$	4976
no. of restraints, params	1, 759
$R(F)_{I>2\sigma I}$[a]	0.0218
$R_w(F)^2_{\text{all data}}$[b]	0.0589
GOF[c]	1.065
Δ/σ	0.002
max, min $\Delta\varrho$, e/Å^3	+0.602, −0.248

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] Goodness of fit (GOF) = $[\sum w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$.

The compound [PPN]**5** was prepared in a similar way (71% yield), with [PPN]**1** as starting material. Anal. Calcd for $C_{85}H_{69}N_3O_8P_2Ru_3Si_2$: C, 60.70; H, 4.13; N, 2.50. Found: C, 61.07; H, 4.13; N, 2.70.

[PPN][$Ru_3(\mu$-dmpz)$(\mu$-$H)_2${Si$(OMe)_3$}$_2(CO)_8$] ([PPN]6). A solution of [PPN]**1** (90 mg, 0.074 mmol) and $HSi(OMe)_3$ (20 μL, 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 × 5 mL) to give [PPN]**6** as an orange air-sensitive oil which could not be crystallized. IR ν(CO) (THF): 2066 (m), 2018 (sh), 2012 (vs), 1984 (s), 1972 (sh), 1952 (m), 1930 (sh) cm^{-1}. ^1H NMR ($CDCl_3$): 7.7−7.3 (m, 30 H, PPN) ppm; 5.28 (s, 1 H), 1.99 (s, 3 H), 1.96 (s, 3 H) (dmpz) ppm; 3.56 (s, 9 H), 3.30 (s, 9 H) (OMe_3) ppm; −11.63 (s, 1 H), −12.34 (s, 1 H) (μ-H) ppm.

[Et_4N][$Ru_3(\mu$-dmpz)$(\mu$-$H)_2(SnBu_3)_2(CO)_8$] ([Et_4N]7). A solution of [Et_4N]**1** (80 mg, 0.099 mmol) and $HSnBu_3$ (67 μL, 0.247 mmol) in THF (20 mL) was stirred at reflux temperature for 1.5 h. The color changed from yellow to violet. The solvent was removed and the residue washed with hexane (3 × 5 mL) to give the complex [Et_4N]**7** as a violet oil which could not be crystallized. IR ν(CO) (THF): 2080 (w), 2006 (s), 1991 (s), 1972 (s), 1926 (s), 1906 (sh) cm^{-1}. ^1H NMR ($CDCl_3$): 5.46 (s, 1 H), 1.99 (s, 6 H) (dmpz) ppm; 3.13 (q, br, 8 H), 1.5−0.8 (m, 66 H) (Et_4N and $SnBu_3$) ppm; −11.09 (s with satellites, J = 28 Hz, 2 H, μ-H) ppm.

The compound [PPN]**7** (violet oil) was prepared in a similar way, with [PPN]**1** as starting material.

[Et_4N][$Ru_3(\mu$-dmpz)$(\mu$-$H)_2(SnPh_3)_2(CO)_8$] ([Et_4N]8). A solution of [Et_4N]**1** (80 mg, 0.099 mmol) and $HSnPh_3$ (74 mg, 0.211 mmol) in THF (20 mL) was stirred at reflux temperature for 2 h. The color changed from yellow to red-violet. The solvent was removed and the residue washed with diethyl ether (2 × 5 mL) to give [Et_4N]**8** as a violet solid (97 mg, 67%). Anal. Calcd for $C_{57}H_{59}N_3O_8Ru_3Sn_2$: C, 47.06; H, 4.09; N, 2.89. Found: C, 46.91; H, 4.23; N, 2.85. IR ν(CO) (THF): 2089 (w), 2031 (vs), 2015 (s), 2000 (sh), 1954 (s, br), 1942 (sh, br) cm^{-1}. ^1H NMR ($CDCl_3$): 7.6−7.0 (m, 30 H, $SnPh_3$) ppm; 5.50 (s, 1 H), 1.54 (s, 6 H) (dmpz) ppm; 2.38 (q, br, 8 H), 0.75 (t, br, 12

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for the Non-H Atoms of [PPN]3

atom	x/a	y/b	z/c	U_{eq}[a]	atom	x/a	y/b	z/c	U_{eq}[b]
Ru(1)	7068(1)	1310(1)	7825(1)	38(1)	P(1)	7257(1)	1447(1)	1559(1)	38(1)
Ru(2)	8021(1)	1937(1)	6919(1)	36(1)	P(2)	7648(1)	1157(1)	3141(1)	36(1)
Ru(3)	8703(1)	−121(1)	7919(1)	37(1)	N(3)	7568(3)	732(5)	2359(2)	47(1)
C(1)	5810(3)	1645(6)	7624(3)	54(1)	C(28)	6095(3)	671(6)	1119(2)	44(1)
O(1)	5076(2)	1926(6)	7489(3)	85(1)	C(29)	5756(4)	−503(6)	1336(3)	63(2)
C(2)	7448(4)	2181(7)	8749(3)	64(2)	C(30)	4875(4)	−908(8)	989(3)	78(2)
O(2)	7671(4)	2734(7)	9269(2)	117(2)	C(31)	4347(4)	−154(9)	431(3)	77(2)
C(3)	7149(3)	3161(6)	7354(3)	56(1)	C(32)	4691(4)	1005(8)	227(3)	77(2)
O(3)	6935(3)	4312(4)	7286(2)	68(1)	C(33)	5564(3)	1436(7)	561(3)	58(1)
C(4)	7801(3)	2289(5)	5961(3)	47(1)	C(34)	7353(3)	2982(5)	1398(2)	43(1)
O(4)	7679(3)	2516(5)	5377(2)	67(1)	C(35)	7978(4)	3488(7)	1104(3)	62(2)
C(5)	8709(3)	3566(5)	7100(2)	45(1)	C(36)	8064(4)	4910(9)	1030(4)	86(2)
O(5)	9148(3)	4546(4)	7221(2)	68(1)	C(37)	7552(5)	5841(8)	1269(4)	86(2)
C(6)	9451(4)	1105(6)	7570(3)	59(1)	C(38)	6929(5)	5334(7)	1555(3)	74(2)
O(6)	10121(2)	1511(5)	7527(3)	75(1)	C(39)	6821(4)	3940(6)	1616(3)	52(1)
C(7)	9341(4)	475(7)	8879(3)	60(1)	C(40)	7909(3)	183(5)	1119(2)	43(1)
O(7)	9713(3)	866(7)	9428(2)	105(2)	C(41)	7558(4)	−162(8)	419(3)	69(2)
C(8)	9486(3)	−1597(6)	7813(3)	52(1)	C(42)	8069(5)	−878(9)	83(3)	81(2)
O(8)	9981(3)	−2351(5)	7710(3)	78(1)	C(43)	8938(4)	−1235(7)	453(3)	68(2)
N(1)	7049(2)	−759(4)	8212(2)	42(1)	C(44)	9287(4)	−890(7)	1145(3)	61(1)
N(2)	7824(2)	−1426(4)	8267(2)	41(1)	C(45)	8786(3)	−180(7)	1483(2)	52(1)
C(9)	7776(4)	−2747(5)	8467(2)	51(1)	C(46)	8653(3)	402(5)	3732(2)	42(1)
C(10)	8532(4)	−3749(7)	8602(3)	72(2)	C(47)	9000(3)	926(6)	4413(2)	56(1)
C(11)	6928(4)	−2926(7)	8535(3)	61(1)	C(48)	9772(4)	330(7)	4867(3)	71(2)
C(12)	6493(3)	−1660(7)	8374(3)	54(1)	C(49)	10184(4)	−735(7)	4653(3)	67(2)
C(13)	5572(4)	−1253(8)	8361(4)	81(2)	C(50)	9850(4)	−1252(7)	3986(3)	64(2)
C(14)	6957(3)	270(4)	6860(2)	35(1)	C(51)	9069(3)	−692(6)	3515(3)	50(1)
C(15)	6073(3)	50(5)	6308(2)	36(1)	C(52)	7727(3)	3017(5)	3301(2)	40(1)
C(16)	5655(3)	1078(6)	5830(2)	49(1)	C(53)	8449(3)	3751(6)	3212(3)	51(1)
C(17)	4810(3)	850(6)	5353(3)	55(1)	C(54)	8505(4)	5150(7)	3301(3)	68(2)
C(18)	4377(3)	−401(6)	5339(3)	53(1)	C(55)	7857(5)	5868(7)	3485(3)	71(2)
C(19)	4782(3)	−1416(6)	5815(3)	49(1)	C(56)	7160(5)	5175(7)	3582(3)	68(2)
C(20)	5614(3)	−1186(5)	6297(2)	44(1)	C(57)	7086(4)	3744(6)	3491(3)	54(1)
C(21)	7740(3)	−407(4)	6901(2)	36(1)	C(58)	6706(3)	531(5)	3386(2)	42(1)
C(22)	7848(3)	−1480(5)	6400(2)	38(1)	C(59)	6818(4)	−162(7)	4018(3)	62(1)
C(23)	7523(3)	−2822(5)	6442(3)	47(1)	C(60)	6062(5)	−577(8)	4184(4)	79(2)
C(24)	7591(3)	−3861(6)	5990(3)	55(1)	C(61)	5213(4)	−326(8)	3727(3)	72(2)
C(25)	8001(4)	−3610(7)	5490(3)	68(2)	C(62)	5114(4)	349(7)	3107(3)	62(2)
C(26)	8354(5)	−2321(7)	5459(3)	73(2)	C(63)	5843(3)	787(6)	2934(3)	51(1)
C(27)	8283(4)	−1257(6)	5913(3)	60(1)					

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

H) (Et_4N) ppm; −10.33 (s with satellites, J = 30 Hz, 2 H, μ-H) ppm. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 205.8, 199.9, 199.5, 199.3, 198.8 (CO) ppm; 146.9, 106.9, 13.6 (dmpz) ppm; 54.6, 7.7 (Et_4N) ppm.

The compound [PPN]**8** was prepared in a similar way (66% yield), with [PPN]**1** as starting material. Anal. Calcd for $C_{85}H_{69}N_3O_8P_2Ru_3Sn_2$: C, 54.80; H, 3.73; N, 2.25. Found: C, 55.08; H, 3.80; N, 2.38.

Reaction of [NEt_4]3 with $HSiPh_3$. A solution of [NEt_4]**3** (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 ^1H NMR spectrum of the solid revealed a mixture of complexes in which [Et_4N]**5** was the major component. A GC analysis of the ethereal solution indicated the presence of *cis*- and *trans*-stilbene. Analogous results were obtained when $HSiEt_3$ was substituted for $HSiPh_3$.

Reaction of [NEt_4]3 with $HSnPh_3$. A solution of [NEt_4]-**3** (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 ^1H NMR spectrum of the solid revealed the presence of [Et_4N]**8**. A GC analysis of the ethereal solution indicated the presence of diphenylacetylene.

Crystal Structure of [PPN]3. 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 $15 < \theta < 20°$. 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.[32] An empirical absorption correction based on ψ-scans was applied;[33] μ(Mo Kα) = 8.99 cm^{-1} (minimum, maximum correction factors 0.945, 1.000). Lorentz and polarization corrections were applied, and data were reduced to $|F_o|$ values.

The structure was solved by Patterson interpretation using DIRDIF92.[34] Isotropic least-squares refinement, using a local version[35] of SHELX,[36] was followed by a semiempirical absorp-

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tion correction[37] (minimum, maximum correction factors 0.28, 0.34). Full-matrix anisotropic least-squares refinement over F^2, using the program SHELXL93,[38] 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 $\sum w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.5332P]$, with $\sigma(F_o)$ from counting statistics and $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors were taken from ref 39. Geometrical calculations were made with PARST.[40] The structure plot was drawn with the EUCLID package.[41] 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.

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Supporting Information Available: Tables of bond distances and angles, anisotropic thermal parameters, and H-atom coordinates for [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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