

Reactivity of [Ru₃(CO)₁₂] with a Phosphine-Functionalized Imidazol-2-ylidene and Its Imidazolium Salt

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The trinuclear cluster $[Ru_3(CO)_{12}]$ reacts at room temperature with the phosphine-functionalized N-heterocyclic carbene (NHC) ligand 1-[2-(diphenylphophino)ethyl]-3-methylimidazol-2-ylidene (dppeImMe), in 1:1 mol ratio, to give the edge-bridged trinuclear derivative $[Ru_3(\mu-\kappa^2 C, P-dppeImMe)(CO)_{10}]$ (1). The use of a 1:3 $[Ru_3(CO)_{12}]$ to dppeImMe mol ratio leads to the mononuclear derivative $[Ru(\kappa^2 C, P-dppeImMe)(CO)_3]$ (2), which has a trigonal-bipyramidal ligand arrangement with the NHC and phosphine fragments of the dppeImMe ligand in axial and equatorial positions, respectively. Upon gentle heating (refluxing THF), compound 1 is transformed into the face-capped dihydrido derivative $[Ru_3(\mu-H)_2(\mu_3-\kappa^3 C_2, P-dppeImCH)(CO)_8]$ (3), which arises from the oxidative addition of two C–H bonds of the N-methyl group of the dppeImMe ligand. The trinuclear salt $[Ru_3(\kappa P-dppeHImMe)_3(CO)_9][BF_4]_3$ ($4[BF_4]_3$), which contains a P-coordinated 1-[2-(diphenylphophino)ethyl]-3-methylimidazolium ligand ([dppeHImMe]]BF4]. The deprotonation of $4[BF_4]_3$ with three equivalents of K[N(SiMe_3)_2] is an alternative way to prepare the mononuclear complex 2.

Introduction

The current interest of the chemical community in the coordination chemistry of N-heterocyclic carbenes (NHC)¹ and in the catalytic properties of many of their complexes² has recently impelled studies on the synthesis and reactivity of transition metal carbonyl clusters containing NHC ligands. Within this field and as far as ruthenium carbonyl cluster complexes are concerned, the pioneering work of Lappert and Pye, who reported the synthesis of [Ru₃(CO)₁₁-(Et₂H₂Im)] (Et₂H₂Im = 1,3-diethylimidazolin-2-ylidene) more

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Scheme 1 shows some representative reactions of 1,3disubstituted imidazol-2-ylidenes (R_2Im) with [$Ru_3(CO)_{12}$]. While 1,3-dimethylimidazol-2-ylidene (Me_2Im) and 1,3-dimesitylimidazol-2-ylidene (Me_2Im) react with [$Ru_3(CO)_{12}$] at room temperature to give normal CO-substitution trinuclear products, [$Ru_3(R_2Im)(CO)_{11}$],⁴ analogous reactions

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with the very bulky NHCs 1,3-di-tert-butylimidazol-2-ylidene (^{*t*}Bu₂Im) and 1.3-diadamantylimidazol-2-ylidene (Ad₂Im) afford CO-substitution products that contain an "abnormally" bound (through C⁴) NHC ligand, $[Ru_3(a-R_2Im)(CO)_{11}]$.¹¹ Mononuclear complexes of the types $[Ru(R_2Im)_2(CO)_3]^{12}$ and $[Ru(R_2Im)(CO)_4]^{13}$ have been obtained using 1:6 or 1:3 cluster to NHC mole ratios, respectively.

Interestingly, as a consequence of the high basicity of the NHC ligands, the clusters $[Ru_3(NHC)(CO)_{11}]$ (NHC = R_2Im , a-R₂Im) undergo easy C-H bond cleavage processes upon thermal activation to give trinuclear hydrido derivatives that contain NHC-derived face-capping ligands, such as [Ru₃(µ-H)₂(μ_3 - $\kappa^2 C_2$ -MeImCH)(CO)₉]⁵ and [Ru₃(μ -H)(μ_3 - $\kappa^2 C_2$ -R₂C₃- $N_2H)(CO)_9]^{11}$ (Scheme 2). An AIM theoretical analysis of the bonding in $[Ru_3(\mu-H)_2(\mu_3-\kappa^2C_2-MeImCH)(CO)_9]^6$ as well as some reactivity⁷ and a DFT mechanistic study of its synthesis from $[Ru_3(Me_2Im)(CO)_{11}]^8$ have been published.

It has been reported that some 1,3-disubstituted imidazol-2-thiones and imidazolium chlorides react with $[Ru_3(CO)_{12}]$ to give NHC cluster derivatives.¹³

Concerning other transition metal cluster complexes, different from triruthenium clusters, NHC derivatives of $[Ru_4(\mu-H)_4(CO)_{12}]$,^{15,16} $[Os_3(CO)_{12}]$,^{4,11b} $[Os_3(\mu-H)_2-(CO)_{10}]$,¹⁶⁻¹⁸ $[Os_3(CO)_{10}(MeCN)_2]$,^{16,18} $[Os_4(\mu-H)_4(CO)_{10}-$



(MeCN)2],19 and some tripalladium20 and mixed-metal MoNi₂²¹ carbonyl clusters have also been described.

On the other hand, although the coordination chemistry of bi-, tri-, or polydentate ligands constituted by at least one NHC moiety has already been extensively studied,²² only two works have hitherto been published involving such ligands and transition metal carbonyl clusters. They describe the synthesis of triruthenium and triosmium clusters containing bidentate NHC-thiolate ligands derived from levamilsolium salts⁹ (Scheme 3) and reactions of NHC-functionalized indenes with $[Ru_3(CO)_{12}]^{14}$ (Scheme 4).

We now describe the preparation of the first [Ru₃(CO)₁₂]derived complexes containing an imidazol-2-ylidene ligand functionalized with a phosphine moiety, namely, 1-[2-(diphenylphosphino)ethyl]-3-methylimidazol-2-ylidene (dppeImMe). We have chosen two different synthetic approaches for this study: (a) to treat $[Ru_3(CO)_{12}]$ with different amounts of dppeImMe and (b) to deprotonate (with a strong base) cationic [Ru₃(CO)₁₂]-derived complexes, previously made by treating $[Ru_3(CO)_{12}]$ with the imidazolium cation $[dppeHImMe]^+$.

The coordination chemistry of phosphine-functionalized imidazol-2-ylidenes has already been studied to a significant extent, but only mononuclear derivatives of these ligands have hitherto been reported.23

Results and Discussion

Reactions of $[Ru_3(CO)_{12}]$ with dppeImMe. The treatment of [Ru₃(CO)₁₂] with an equimolar amount of dppeHImMe (prepared in situ by deprotonating [dppeHImMe][BF₄] with K[N(SiMe₃)₂]) in THF at room temperature led to the trinuclear cluster [Ru₃(μ - $\kappa^2 C$, *P*-dppeImMe)(CO)₁₀] (1), which was isolated as a dark orange solid after a chromatographic workup (Scheme 5).

The X-ray structure of compound 1 is shown in Figure 1. A selection of bond distances is given in Table 1. The structure can be described as resulting from the substitution of a

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dppeImMe ligand for two equatorial CO groups of different Ru atoms of $[Ru_3(CO)_{12}]$, thus spanning an Ru–Ru edge. The coordination of the dppeImMe ligand does not alter significantly the Ru–Ru distances with respect to those of $[Ru_3(CO)_{12}]$,²⁴ since in compound 1 they range from 2.8694(4) to 2.8855(4) Å. The Ru–C_{carbene} distance, Ru2–C1 2.100(4) Å, is a bit shorter than that found in

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Figure 1. Structure of compound **1** (ellipsoids set at 20% probability; phenyl hydrogen atoms omitted for clarity).

Table 1. Selected Interatomic Distances	(Å	(A) in Compound 1
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Ru1-Ru2	2.8855(4)	C3-N1	1.384(5)
Ru1-Ru3	2.8863(4)	C4-N1	1.451(5)
Ru2-Ru3	2.8694(4)	C4-C5	1.528(5)
C1-Ru2	2.100(4)	C5-P1	1.843(4)
C1-N1	1.365(5)	C6-N2	1.450(6)
C1-N2	1.354(4)	P1-Ru1	2.3419(9)
C2-C3	1.342(7)	C-O (av)	1.136(7)
C2-N2	1.395(6)	C _(CO) -Ru (av)	1.92(2)

[Ru₃(Me₂Im)(CO)₁₁], 2.115(4) Å,⁴ while the Ru–P distance, Ru1–P1 2.3419(9) Å, is slightly shorter than that of [Ru₃-(PPh₃)(CO)₁₁],²⁵ 2.379(4) Å, but slightly longer than those of [Ru₃(μ - $\kappa^2 P_2$ -dppe)(CO)₁₀] (dppe = 1,2-bis(diphenylphosphino)ethane), 2.330(1) and 2.283(2) Å.²⁶

The solution IR and NMR spectroscopic data of compound 1 are in harmony with its solid-state structure. The absorptions of terminal CO ligands are the only signals observed in the stretching carbonyl region of its IR spectrum. The ¹³C and ³¹P NMR spectra of 1 show the resonances of the C_{carbene} and P atoms at 172.8 and 42.3 ppm, respectively.

In an attempt to introduce more than one dppeImMe ligand into a triruthenium cluster, the parent carbonyl [Ru₃-(CO)₁₂] was treated with three equivalents of dppeImMe in THF at room temperature. The mononuclear ruthenium(0) derivative [Ru($\kappa^2 C$,*P*-dppeImMe)(CO)₃] (2) was the only product of this reaction (Scheme 5). The use of a 1:2 [Ru₃-(CO)₁₂] to dppeImMe mol ratio led to a mixture of products that could not be satisfactorily separated.

The composition of compound **2** was established by analytical and spectroscopic techniques. Its IR spectrum (recorded in THF) displays a very strong band centered at 1833 cm⁻¹ accompanied by two strong bands at higher frequencies, 1998 and 1909 cm⁻¹. The low wavelengths of these absorptions provide convincing evidence for the presence of a strongly basic ligand within the metal coordination shell. This three-band ν_{CO} pattern is coherent with an axial–equatorial coordination of the ligand in a trigonal-bipyramidal (tbp) complex (C_s symmetry), as has been observed for [M($\kappa^2 P_2$ -P–P)(CO)₃] (M = Fe, Ru; P–P = chelating diphosphine),²⁷ but it gives no hint about what ligand atom (P or C) is in each coordination of the ligand in a square-base pyramidal (sbp)

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complex (also of C_s symmetry). The room-temperature NMR spectra of **2** confirm the presence of the dppeImMe ligand in the complex (the resonances of the C_{carbene} and P atoms are observed at 176.3 and 30.0 ppm in their respective spectra) and also indicate that the complex is fluxional in solution, since only one resonance, at 214.2 ppm (d, $J_{C-P} = 9$ Hz), is observed for the carbonyl ligands in the ¹³C{¹H} spectrum. The fluxionality could not be frozen out even upon cooling to -80 °C. Therefore, the IR and NMR spectra of compound **2** do not provide enough data to unequivocally assign a structure to this complex.

As we could not get crystals of compound 2 suitable for an X-ray diffraction study, DFT calculations were carried out to shed more light on the structure of this complex. Structure optimization calculations were performed using input models of tbp and sbp geometries having all possible ligand arrangements. They all converged to one of the tbp structures shown in Figure 2, **2ax** or **2eq**. As the calculations indicated that structure **2ax** is more stable than structure **2eq** ($\Delta E = 7.2 \text{ kcal mol}^{-1}$, $\Delta G = 7.1 \text{ kcal mol}^{-1}$, $\Delta H = 6.9 \text{ kcal mol}^{-1}$) and as compound **2** is fluxional in solution (even at very low temperature), we conclude that, in the solid state, compound **2** should have the structure **2ax**, which is a tbp ligand arrangement with the NHC and phosphine fragments of the dppeImMe ligand in axial and equatorial positions, respectively.

With the only exception of $[Ru({}^{1}Pr_{2}Im)_{2}(CO)_{3}]$ and $[Ru({}^{1}Pr_{2}ImMe_{2})_{2}(CO)_{3}]$, which contain isopropyl groups on the N atoms and have an axial-equatorial arrangement of the NHCs in a tbp ligand environment, ¹² all the remaining complexes of the types $[Ru(NHC)_{2}(CO)_{3}]$ (NHC = Et₂-ImMe₂, ¹² Mes₂Im, ²⁸ Cy₂Im²⁸) and $[Ru(PR_{3})_{2}(CO)_{3}]^{29}$ known at this moment have a tbp axial-axial ligand array of the non-carbonyl ligands. An analogous tbp axial-axial ligand arrangement has also been observed in the mixed NHC phosphine complex $[Ru(Mes_{2}Im)(PPh_{3})(CO)_{3}]$.³⁰

As far as we are aware, only one work reporting the synthesis of ruthenium(0) complexes having a bidentate NHC-phosphine ligand has hitherto been published. It describes the preparation of $[\text{Ru}(\kappa^2 C, P\text{-dppeImR})(\text{PPh}_3)\text{-}(\text{CO})_2]$ (R = Mes, Dipp) from dppeImR and the mononuclear complex $[\text{Ru}(\text{PPh}_3)_3(\text{CO})_2]$, but the structures of these compounds have not been unambiguously determined.^{23b}

Thermolysis of Compound 1. Heating to reflux a THF solution of complex 1 for 20 min led to its quantitative transformation into the face-capped trinuclear derivative



Figure 2. DFT-optimized structures, at the B3LYP/LanL2DZ/ 6-31G(d,p) level of theory, of the two possible tbp isomers of compound **2**.



Figure 3. Structure of compound **3** (ellipsoids set at 30% probability; phenyl hydrogen atoms omitted for clarity).

Table 2. Selected Interatomic Distances (Å) in Compound 3

			-
Ru1-Ru2	2.8253(3)	C4-N1	1.457(3)
Ru1-Ru3	2.7931(3)	C4-C5	1.529(3)
Ru2-Ru3	3.0530(3)	C5-P1	1.856(2)
C1-Ru2	2.063(2)	C6-N2	1.453(3)
C1-N1	1.349(3)	C6-Ru1	2.116(3)
C1-N2	1.342(3)	C6-Ru3	2.139(3)
C2-C3	1.348(4)	P1-Ru2	2.3331(6)
C2-N2	1.385(3)	C-O (av)	1.138(7)
C3-N1	1.394(3)	$C_{(CO)}$ -Ru (av)	1.92(3)

Scheme 6



 $[Ru_3(\mu-H)_2(\mu_3-\kappa^3C_2,P-dppeImCH)(CO)_8]$ (3), which was isolated as an orange solid (Scheme 6).

The molecular structure of **3** was determined by X-ray diffraction (Figure 3, Table 2). The molecule contains a dppeImCH ligand capping a face of the ruthenium triangle in such a way that the Ru1–Ru3 edge is spanned by the CH fragment, while the remaining metal atom, Ru2, is chelated by the bridging ligand through the carbene C atom and the phosphine fragment P atom. Two edges of the metal triangle, Ru1–Ru3 and Ru2–Ru3, are also spanned by hydride

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ligands. The length of the hydride-unbridged edge, Ru1–Ru2 2.8253(3) Å, is intermediate between those of the hydridebridged edges, Ru1–Ru3 2.7931(3) Å, Ru2–Ru3 3.0530(3) Å. The cluster shell is completed by eight carbonyl ligands.

The solution IR and NMR spectra of **3** are in complete agreement with its solid-state structure. The IR spectrum clearly shows that this complex has only terminal CO ligands. The NMR resonances of the C_{carbene} and P atoms of **3** are observed at 173.9 (doublet, $J_{C-P} = 13$ Hz) and 28.6 ppm in their respective spectra. In addition to the resonances of the dppmIm fragment, the ¹H NMR spectrum of **3** also contains the resonances of two hydrides (at -12.19 and -16.76 ppm) and an aliphatic CH proton (at 6.74 ppm).

The process that activates two C-H bonds of the N-methyl group of 1 to give 3 should be related to that that transforms the clusters $[M_3(Me_2Im)(CO)_{11}]$ (M = Ru, Os) into $[M_3(\mu-H)_2(\mu_3-\kappa^2C_2-MeImCH)(CO)_9]^5$ whose mechanism, which has been studied by DFT methods, proceeds through an edge-bridged monohydrido intermediate, $[M_3(\mu-H) (\mu - \kappa^2 C_2 - \text{MeImCH}_2)(\text{CO})_{10}]$.⁸ It is now clear that the high basicity of the NHCs not only enhances the basicity of the metal atoms to which they are attached, increasing their tendency to get involved in oxidative addition processes, but also facilitates the elimination of one or more CO groups from the initial cluster under mild conditions. These facts, the high probability that a ligand C-H bond be placed in close proximity to a metal atom in a cluster, and the irreversibility of the CO elimination steps, explain the easy metalation of C-H,^{5,10,11} C-C,^{7b} or C-N^{7b} bonds in carbonyl cluster complexes that contain NHC ligands.

The structure of compound **3** resembles that of $[Ru_3(\mu-H)_2(\mu_3-\kappa^3C,N_2-MebipyCH)(CO)_8]$, which arises from the reaction of $[Ru_3(CO)_{12}]$ with 6,6'-dimethyl-2,2'-bipyridine (Me₂bipy). In this case, the chelation of the rigid Me₂bipy ligand to a cluster metal atom places a ligand methyl group in close proximity to one or more metal atoms, thus favoring its metalation.³¹ Noting that the dppeImMe ligand of compound **1** bridges an Ru–Ru edge whereas the C_{carbene} and P atoms of the dppeImCH ligand of **3** are attached to the same



Figure 4. Structure of the cation of compound $4[BF_4]_3$ viewed along the C_3 symmetry axis (ellipsoids set at 20% probability; hydrogen atoms omitted for clarity).

Table 3. Selected Interatomic Distances (A	L)) in	Com	pound	4	BF	4	13
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Ru-Ru	2.858(2)	C4-C5	1.50(2)
C1-N1	1.32(2)	C5-P1	1.85(1)
C1-N2	1.34(2)	C6-N2	1.46(2)
C2-C3	1.31(2)	P1-Ru1	2.351(4)
C2-N2	1.39(2)	C-O (av)	1.17(3)
C3-N1	1.38(2)	$C_{(CO)}$ -Ru (av)	1.89(3)
C4-N1	1.46(2)		

metal atom, it is not clear whether the chelating ability of dppeImMe contributes to promote the methyl C-H bond activation processes because this ligand is not as rigid as Me₂bipy and, in the transformation of **1** into **3**, the bridging to chelating transformation of the ligand may occur before or after the C-H bond activation processes. The fact that the CO groups of **1** are fluxional in solution would facilitate the rearrangement of the dppeImMe ligand over the Ru₃ triangle.

Reactions of $[Ru_3(CO)_{12}]$ with the Imidazolium-Phosphine Salt [dppeHImMe][BF₄]. No reaction was observed when $[Ru_3(CO)_{12}]$ was treated with various amounts of [dppeHImMe][BF₄] in THF at room temperature. However, upon heating to reflux temperature and regardless of the ratio of the reactants, the trisubstituted product $[Ru_3(\kappa P\text{-dppeHI-}$ $mMe)_3(CO)_9][BF_4]_3$ (4[BF₄]_3) precipitated out of the solution as a violet solid (Scheme 7). The use of [dppeHImMe]-[BF₄] to $[Ru_3(CO)_{12}]$ ratios smaller than 3 led to mixtures of $[Ru_3(CO)_{12}]$ and 4[BF₄]_3.

The solid-state structure of $4[BF_4]_3$ was determined by X-ray diffraction (Figure 4, Table 3). The structure is of poor quality (see the Experimental Section), but it unequivocally provides the atom connectivity. The cation has C_3 symmetry and consists of three symmetry-related Ru(κP -dppeHIm-Me)(CO)₃ units interconnected by Ru–Ru bonds. The cationic [dppeHImMe]⁺ ligands, which occupy equatorial coordination sites, are coordinated through the P atom. The NMR spectra of $4[BF_4]_3$ corroborate that these structural features are maintained in solution. The carbonyl absorptions of the IR spectrum appear at relatively low wave numbers (2045–1968 cm⁻¹), indicating that the positive charge of the imidazolium fragment does not affect much the basicity of the phosphine moiety. A few structures of

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neutral triruthenium complexes of the type $[Ru_3(\kappa P-PR_3)_3-(CO)_9]$ have been crystallographically determined, and they all have a local C_3 symmetry.³²

Therefore, the chemical behavior of the cationic [dppeHI-mMe]⁺ ligand parallels that of neutral phosphine ligands, which easily lead to trisubstituted derivatives when they react with [Ru₃(CO)₁₂] upon thermal activation.³³

Deprotonation of $[Ru_3(\mathcal{K}P\text{-}dppeHImMe)_3(CO)_9][BF_4]_3$ (4[BF₄]_3). As the deprotonation of imidazolium salts with strong bases usually leads to NHC derivatives,¹ we reasoned that the treatment of compound 4[BF₄]_3 with a strong base could be either an entry to triruthenium clusters containing more than one dppeImMe ligand or an alternative way to synthesize the mononuclear complex 2, which, as described above, can be prepared from the reaction of [Ru₃(CO)₁₂] with three equivalents of dppeImMe.

As shown in Scheme 7, the reaction of $4[BF_4]_3$ with three equivalents of $K[N(SiMe_3)_2]$ led to the immediate formation of the mononuclear derivative 2 in quantitative yield. Therefore, Ru-Ru bond cleavage processes accompany the coordination of the pendant NHC ligand fragments that are formed by deprotonation of the imidazolium rings of 4- $[BF_4]_3$. Mixtures of products, which were not separated, were obtained when less than three equivalents of $K[N(SiMe_3)_2]$ was used.

It is already known that the great basicity and volume of monodentate NHC ligands favor the cleavage of Ru–Ru bonds over Ru–CO bonds in triruthenium clusters (Scheme 1).^{12,13} This work now demonstrates that bidentate NHC-phosphine ligands also follow this trend.

Concluding Remarks

In this paper, we have described the synthesis of the first trinuclear clusters to contain phosphine-functionalized NHC ligands. We have used dppeImMe as a representative ligand of this kind. While the dppeImMe ligand prefers to bridge a cluster edge when it is the only non-carbonyl ligand in the cluster (as in complex 1), it prefers to chelate a metal atom when more ligands are attempted to introduce into the cluster. However, all attempts to prepare triruthenium clusters containing more than one dppeImMe ligand induces the cleavage of Ru–Ru bonds, as indicated by the fact that the mononuclear derivative **2** was obtained either by treating [Ru₃(CO)₁₂] with three equivalents of dppeImMe or by deprotonating **4**[BF₄]₃.

The dppeImMe ligand is basic enough to promote its easy degradation upon mild thermal activation, via an intramolecular cleavage of two C-H bonds of its N-methyl group (transformation of 1 into 3). These C-H bond activation

processes are also facilitated by the structure of the ligand, which allows the approach of the N-methyl group to the metal atoms.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) or CaH₂ (dichloromethane) 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 on silica gel. The imidazolium bromide [dppeHImMe]Br was prepared as described elsewhere.^{23k} All remaining starting reagents were purchased from commercial sources. All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run on a Bruker DPX-300 instrument, using CH₂Cl₂ as internal standard for ¹H ($\delta = 5.32$), CD_2Cl_2 as internal standard for ¹³C ($\delta = 53.8$), and aqueous 85% H_3PO_4 as external standard ($\delta = 0.00$). Microanalyses were obtained from the University of Oviedo Analytical Service. FAB mass spectra were obtained from the University of A Coruña Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

Synthesis of [dppeHImMe][BF4]. A saturated aqueous solution of Na[BF₄] was dropwise added to a solution of [dppeHImMe]Br (5.9 g mg, 0.16 mol) in methanol (25 mL) until the complete precipitation of a white solid was observed. The solvent mixture was removed under reduced pressure, and the residue was extracted into dichloromethane (3 \times 30 mL). The combined extracts were dried with anhydrous MgSO₄, and the resulting solution was evaporated to dryness to give a white solid, which was washed with diethyl ether $(2 \times 20 \text{ mL})$ and dried under vacuum (5.5 g, 91%). Anal. Calcd for $C_{18}H_{20}BF_4N_2P$ (382.15): C, 56.57; H, 5.28; N, 7.33. Found: C, 56.62; H, 5.38; N, 7.27. ¹H NMR (CD₂Cl₂, 293 K): δ 8.68 (s, 1 H), 7.49 (m, 4 H), 7.32 (m, 6 H), 7.32 (s, br, 1 H), 7.25 (s, br, 1 H), 4.33 (m, 2 H), 3.81 (s, 3 H), 2.73 (m, 2 H). ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂, 293 K): $\delta -21.7. {}^{13}C{}^{1}H{}$ and DEPT NMR (CD₂Cl₂, 293 K): δ 136.9 (d, J = 12 Hz, C), 136.5 (s, CH), 133.1 (d, J = 20 Hz, CH), 129.8 (s, CH), 129.3 (d, J = 7 Hz, CH), 124.1 (s, CH), 122.7 (s, CH), 48.1 $(d, J = 24 Hz, CH_2), 36.5 (s, CH_3), 28.9 (d, J = 16 Hz, CH_2).$

Synthesis of $[Ru_3(\mu-\kappa^2 C, P-dppeImMe)(CO)_{10}]$ (1). A toluene solution of K[N(SiMe₃)₂] (500 µL, 0.5 M, 0.250 mmol) was added to a suspension of [dppeHImMe][BF₄] (87 mg, 0.227 mmol) in THF (30 mL). After stirring for 30 min, finely powdered [Ru₃(CO)₁₂] (140 mg, 0.219 mmol) was added. The mixture was stirred for an additional 1 h. The color changed from orange to red. The solvent was removed under reduced pressure and the crude reaction mixture separated by column chromatography on neutral alumina (activity IV, 2×15 cm). Hexane eluted a small amount of [Ru₃(CO)₁₂]. Hexanedichloromethane (3:2) eluted compound 1, which was isolated as a dark orange solid (94 mg, 49%). Anal. Calcd for C₂₈H₁₉-N₂O₁₀PRu₃ (877.65): C, 38.32; H, 2.18; N, 3.19. Found: C, 38.37; H, 2.25; N, 3.05. (+)-FAB-MS: *m*/*z* 879 [M]⁺. IR (THF): $\nu_{\rm CO}$ 2093 (w), 2073 (m), 2038 (w), 2029 (s), 1998 (vs), 1989 (vs), 1966 (w), 1942 (m). ¹H NMR (CD₂Cl₂, 293 K): δ 7.63–7.44 (m, 5 H), 7.38–7.24 (m, 3 H), 7.11 (d, J = 1.7 Hz, 1 H), 7.06 (d, J = 1.7 Hz, 1 H), 6.77 (d, J = 7.8 Hz, 1 H), 6.75 (d, J = 7.8 Hz, 1 H),4.36 (m, 1 H), 4.13 (m, 1 H), 3.84 (s, 3 H), 2.40 (m, 1 H), 2.12 (m, 1 H). ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 293 K): δ 42.3 (s). ${}^{13}C{}^{1}H$ and DEPT NMR (CD₂Cl₂, 293 K): δ 212.4 (br, CO), 172.8 (s, C), 132.0-127.2 (m), 124.3 (s, CH), 120.8 (s, CH), 49.2 (d, J = 6 Hz, CH_2), 39.6 (s, CH_3), 2.6 (d, J = 24 Hz, CH_2).

Synthesis of $[Ru(\kappa^2 C, P-dppeImMe)(CO)_3]$ (2). A toluene solution of K $[N(SiMe_3)_2]$ (4 mL, 0.5 M, 2.000 mmol) was added to a suspension of [dppeHImMe][BF₄] (672 mg, 1.760 mmol) in THF (30 mL). After stirring for 30 min, finely powdered

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Table 4. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-ray Diffraction

	1 3		$4[BF_4]_3$		
formula	$C_{28}H_{19}N_2O_{10}PRu_3$	$C_{26}H_{19}N_2O_8PRu_3$	$C_{63}H_{60}B_3F_{12}N_6O_9P_3Ru_3$		
fw	877.63	821.61	1701.72		
cryst syst	monoclinic	orthorhombic	trigonal		
space group	$P2_1/n$	Pbca	$P-3C_1$		
a, Å	11.5695(1),	14.0159(1)	14.825(1)		
b, Å	15.2004(1)	17.3425(2)	14.825(1)		
<i>c</i> , Å	17.9373(1)	23.5717(2)	41.080(3)		
$\alpha, \beta, \gamma, \text{deg}$	90, 105.220(1), 90	90, 90, 90	90, 90, 120		
V. Å ³	3043.83(4)	5729.59(9)	7819.0(9)		
Z	4	8	4		
<i>F</i> (000)	1712	3200	3408		
$D_{\rm calcd}$, g cm ⁻³	1.915	1.905	1.446		
μ (Cu K α), mm ⁻¹	12.917	13.615	5.920		
cryst size, mm	0.27 imes 0.20 imes 0.08	0.10 imes 0.08 imes 0.05	0.09 imes 0.07 imes 0.03		
T, K	293(2)	293(2)	293(2)		
θ range, deg	3.87 to 73.95	3.15 to 73.88	3.23 to 73.82		
min./max. h, k, l	-12/14, -18/18, -21/20	-17/17, -21/21, -29/27	-14/0, 0/16, 0/46		
no. collected reflns	11 147	61 252	3860		
no. unique reflns	5914	5796	3860		
no, reflns with $I > 2\sigma(I)$	5406	5699	2702		
no. params/restraints	398/0	369/0	316/83		
GOF on F^2	1.045	1.096	1.044		
R_1 (on $F, I > 2\sigma(I)$)	0.0374	0.0242	0.0962		
wR_2 (on F^2 , all data)	0.1084	0.0634	0.2964		
max./min. $\Delta \rho$, e Å ⁻³	-0.984/1.010	-0.715/0.640	-1.030/1.350		

[Ru₃(CO)₁₂] (376 mg, 0.588 mmol) was added. The mixture was stirred for 2 h. The color changed from orange to yellow. The solid of the resulting suspension was filtered off, and the filtrate was evaporated to dryness to give a yellow solid, which was washed with hexane (3 \times 20 mL) and vacuum-dried (695 mg, 82%). Anal. Calcd for C₂₁H₁₉N₂O₃PRu (479.44): C, 52.61; H, 3.99; N, 5.84. Found: C, 52.68; H, 4.03; N, 5.79. IR (THF): ν_{CO} 1998 (s), 1909 (s), 1883 (vs). ¹H NMR (CD₂Cl₂, 293 K): δ 7.68 (m, 4 H), 7.52-7.40 (m, 6 H), 7.02 (d, J = 1.6 Hz, 1 H), 6.93 (d, J = 1.6 Hz, 1 Hz), 6.93 (d, J = 1.6 Hz, 1 Hz), 6.93 (d, J = 1.6 Hz, 1 Hz), 6.93 (d, J =J = 1.6 Hz, 1 H), 4.07 (m, 1 H), 4.00 (m, 1 H), 3.97 (s, 3 H), 2.52 (m, 2 H). ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂, 293 K): δ 30.0 (s). ${}^{13}C{}^{1}H{}$ and DEPT NMR (CD₂Cl₂, 193 K): δ 214.2 (d, J = 9 Hz, CO), 176.3 (d, J = 16 Hz, C), 139.4 (d, J = 32 Hz, C), 132.4 (d, J = 14Hz, CH), 129.3 (s, CH), 128.3 (d, J = 10 Hz, CH), 122.6 (s, CH), 121.7 (s, CH), 47.9 (d, J = 10 Hz, CH₂), 39.6 (s, CH₃), 28.8 (d, $J = 20 \text{ Hz}, CH_2$).

Synthesis of $[Ru_3(\mu-H)_2(\mu_3-\kappa^3C_2,P-dppeImCH)(CO)_8]$ (3). A THF solution (30 mL) of compound 1 (24 mg, 0.029) was stirred at reflux temperature for 20 min. No color change was observed. The solvent was removed under reduced pressure, and the solid residue was washed with hexane $(2 \times 15 \text{ mL})$ to give compound 3 as an orange solid (19 mg, 85%). Anal. Calcd for C₂₆H₁₉N₂O₈₋ PRu₃ (821.63): C, 38.01; H, 2.33; N, 3.41. Found: C, 38.32; H, 2.47; N, 3.09. (+)-FAB-MS: m/z 822 [M – H]⁺. IR (THF): ν_{CO} 2079 (m), 2065 (w), 2038 (vs), 2009 (s), 2000 (s), 1972 (m), 1954 (w). ¹H NMR (CD₂Cl₂, 293 K): δ 7.74–7.64 (m, 3 H), 7.58–7.50 (m, 3 H), 7.48-7.39 (m, 4 H), 7.05 (s, br, 1 H), 6.92 (d, J = 1.6Hz, 1 H), 6.51 (s, 1 H), 4.22 (ddt, J = 32.1, 14.3, 3.6 Hz, 1 H), 3.98 (m, 1 H), 3.06 (m, 1 H), 1.96 (m, 1 H), -12,19 (s, br, 1 H, μ -H), -16.76 (s, br, 1 H, μ -H). ³¹P{¹H} NMR (CD₂Cl₂, 293 K): δ 28.6 (s). ¹³C{¹H} and DEPT NMR (CD₂Cl₂, 293 K): δ 206.5 (d, J = 4 Hz, CO); 205.3 (d, J = 7 Hz, CO); 202.4 (s, CO), 202.1 (s, CO); 193.7 (s, CO); 193.6 (s, CO); 188.4 (d, J = 8 Hz, CO); 186.0 (s, CO), 173.9 (d, J = 13 Hz, C); 131.6 (d, J = 12 Hz, CH); 130.0 (d, J = 24 Hz, C); 128.8 (d, J = 9 Hz, CH), 128.5 (d, J = 10 Hz, CH), 118.6 (s, CH), 118.10 (s, CH), 107.2 (s, CH), 47.0 (s, CH_2), 29.4 (d, J = 27 Hz, CH_2).

Synthesis of [Ru₃(KP-dppeHImMe)₃(CO)₉][BF₄]₃ (4[BF₄]₃). A mixture of [dppeHImMe][BF₄] (130 mg, 0.340 mmol) and finely powdered [Ru₃(CO)₁₂] (72 mg, 0.113 mmol) was stirred in THF (30 mL) at reflux temperature for 1 h. The color changed from orange to dark violet. After cooling to room temperature, the solid was filtered, washed with hexane $(2 \times 20 \text{ mL})$, and

vacuum-dried (77 mg, 40%). Anal. Calcd for C63H60B3F12-N₆O₉P₃Ru₃ (1701.75): C, 44.47; H, 3.55; N, 4.94. Found: C, 44.53; H, 3.63; N, 4.88. IR (CH₂Cl₂): v_{CO} 2045 (w), 2023 (w), 1981 (vs), 1968 (vs). ¹H NMR (CD₂Cl₂, 293 K): δ 8.67 (s, br, 1 H), 7.56–7.45 (m, 10 H), 7.17 (m, 1 H), 7.06 (m, 1 H), 4.09 (m, 2 H), 3.91 (s, 3 H), 3.14 (m, 2 H). ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 293 K): δ 21.9 (s). ¹³C{¹H} and DEPT NMR (CD₂Cl₂, 293 K): δ 136.9 (s, CH), 134.8 (d, J = 43 Hz, C), 132.4 (d, J = 11 Hz, CH), 131.0 (CH), 129.3 (d, J = 10 Hz, CH), 123.9 (CH), 122.4 (CH), 46.1 (d, J = 5 Hz, CH_2), 36.7 (CH_3), 34.0 (d, J = 20 Hz, CH_2).

Deprotonation of 4[BF₄]₃**.** A suspension of 4[BF₄]₃ (616 mg, 0.362 mmol) in THF (30 mL) was treated with a toluene solution of K[N(SiMe₃)₂] (2.3 mL, 0.5 M, 1.150 mmol). Immediately, the solid dissolved to give a yellow solution. An IR analysis of this solution indicated the complete transformation of 4[BF₄]₃ into compound **2**.

Computational Details. The optimized structures were calculated by hybrid DFT, within the GAUSSIAN-03 program suite, ³⁴ using Becke's three-parameter hybrid exchange-correlation functional³⁵ and the B3LYP nonlocal gradient correction.³⁶ The LanL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.³⁷ The basis set used for the remaining atoms was the standard 6-31G with addition of (d,p)-polarization. To determine the structure of compound 2,

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input models corresponding to all possible tbp and sbp ligand arrangements were constructed. After optimization, they all converged to either **2ax** or **2eq**, which were confirmed as energy minima by calculation of analytical frequencies. The energies given in this article are potential energies calculated in the gas phase.

X-ray Diffraction Analyses. Crystals of 1, 3, and 4[BF₄]₃ were analyzed by X-ray diffraction methods. A selection of crystal, measurement, and refinement data is given in Table 4. Diffraction data were collected on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu K α radiation. Empirical absorption corrections for 1 and 3 were applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlisPro RED.³⁸ The XABS2³⁹ empirical absorption correction was applied for 4[BF₄]₃. The structures were solved by Patterson interpretation using the program

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(45) Farrugia, L. J. WinGX, version 1.80.05 (2009). J. Appl. Crystallogr. 1999, 32, 837. DIRDIF.⁴⁰ Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL.41 All non-H atoms were refined anisotropically except for one of the tetrafluoridoborate units of $4[BF_4]_3$. The positions of the hydride atoms of 3 were calculated with XHYDEX.42 The remaining hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The refinement of 4[BF₄]₃ converged with a high discrepancy index ($R_1 = 0.0989$), which is attributed to disorder and high thermal motion of two of the [BF₄]⁻ anions and to the presence of residual electron density arising from a small amount of disordered solvent (dichloromethane). Most of this residual electron density was removed with the PLATON SQUEEZE43 routine to give the final model of 4[BF₄]₃, which, despite its low resolution, unequivocally provides the atom connectivity. The molecular plots were made with the PLATON program package.44 The WINGX program system45 was used throughout the structure determinations. CCDC deposition numbers: 805137 (1), 805138 (3), and 805139 (4[BF₄]₃).

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Supporting Information Available: Atomic coordinates of the structures optimized by DFT calculations and crystallographic data in CIF format for 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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