Organometallics **2001,** *20,* 3821−3824 3821

Synthesis of the Metal-Containing Dinitrile Ligand *trans*-$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CCN\}_2}]$ as a Precursor of Polymetallic Species[†]

Marta E. G. Mosquera, Javier Ruiz,* and Víctor Riera

Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, 33071 Oviedo, Spain

Santiago García-Granda and M. R. Díaz

Departamento de Química Física y Analítica, Universidad de Oviedo, 33071 Oviedo, Spain

Claudette Bois

Laboratoire de Chimie des Metaux de Transition, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France

Received March 26, 2001

Summary: The complex trans-$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CCN\}_2}]$ *(**2**) has been prepared by reaction of trans-*$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CH\}_2}]$ *with* $\mathrm{(CN)_2}$*. **2** behaves as a dinitrile metalloligand, allowing the synthesis of the new polymetallic species trans-*$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CCN{-}Au(PPh_3)\}_2}]^{2+}$ *(**3**), trans-*$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CCN{-}RuCl_2(C_6H_6)\}_2}]$ *(**4**), and trans-*$[\mathrm{Ru(CN^tBu)_2\{(Ph_2P)_2CCN{-}Cu{-}NCC(Ph_2P)_2\}}]_n{}^+$ *(**5**), when treated with the appropriate metallic fragment.*

Introduction

Diphosphinomethanide ligands $\{\mathrm{(PR_2)_2CH}\}^-$ possess a fertile coordination chemistry due to their character as six-electron donors and to the presence of three coordination centers. Hence a rich chemistry has been developed around diphosphinomethanides, leading to the preparation of an important number of derivatives with transition metals, main group elements, and lanthanides.[1] This kind of derivative displays remarkable features such as a variety of coordination modes (mono-, bi-, and tridentate through the carbon and phosphorus donor atoms), high coordination numbers, and, on occasion, stabilization of molecules with elements in low oxidation states such as silicon(II).[2]

Together with this interesting structural behavior, these ligands possess an important synthetic potential. When coordinated by the two phosphorus atoms, it is possible to transform chemoselectively the central carbon atom, leading to the synthesis of new functionalized diphosphines.[3] In particular, the studies of the reactivity with halogens have proved to be very successful, leading to the formation of halodiphosphinomethanides that show a rich and unexpected reactivity.[4] The extension of these reactions to pseudohalogen molecules such as $\mathrm{(CN)_2}$ has allowed us to obtain the complex *fac*-$[\mathrm{Mn(CN^tBu)(CO)_3\{(PPh_2)_2CCN\}}]$, which presented an additional coordination ability through the nitrogen atom, thus being a valuable substrate for the preparation of heterometallic species.[5]

Using a similar experimental approach, we have now succeeded in the synthesis of *trans*-$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CCN\}_2}]$ (**2**), which contains two mutually *trans* cyanodiphosphinomethanide ligands. The potential bidentate nature of this derivative makes it a suitable metalloligand for the synthesis of polymetallic species, as described throughout this paper.

Results and Discussion

The reaction of the compound *trans*-$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CH\}_2}]$[1j] with cyanogen led to the formation of the complexes *trans*-$[\mathrm{Ru(CN^tBu)_2(dppm)\{(PPh_2)_2CCN\}}]^+$ (**1**) and *trans*-$[\mathrm{Ru(CN^tBu)_2\{(PPh_2)_2CCN\}_2}]$ (**2**). A certain amount of the derivative *trans*-$[\mathrm{Ru(CN^tBu)_2(dppm)_2}]^{2+}$ was produced as well (Scheme 1).[10]

This mixture appears to be the result of the heterolytic cleavage of the $\mathrm{(CN)_2}$ molecule promoted by the

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[†] Dedicated to Prof. R. Usón on the occasion of his 75th birthday.

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10.1021/om010243f CCC: $20.00
Publication on Web 07/24/2001

Scheme 1

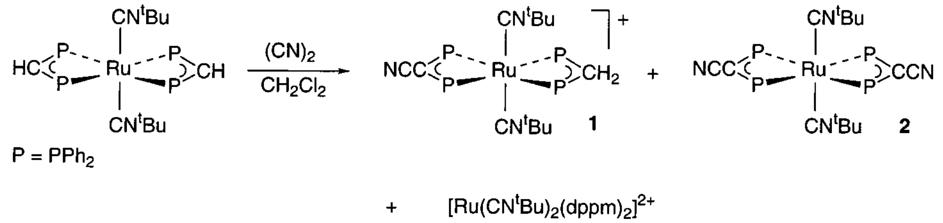

Table 1. Selected IR and RMN Data for Compounds 1−5

compd	ν(CN)[a] (cm^{-1})	^{31}P{^{1}H} NMR[b] (δ, ppm; J, Hz)	^{1}H NMR[b] (δ, ppm; J, Hz)
1	2147	δ_A: −7.8, δ_B: −10.9 $J_{AA'} = 31$, $J_{AB'} = 230$ $J_{AB} = -15$, $J_{BB'} = -10$	5.2 (t, 2H, CH$_2$, $^2J_{PH} = 8$) 0.4 (s, 18H, CH$_3$, ^{t}Bu)
2	2137	−6.6 (s)	0.2 (s, 18H, CH$_3$, ^{t}Bu)
3	2145 (f), 2156 (sh)	29.9 (s, 2P, AuPPh$_3$) −5.1 (s, 4P, PPh$_2$)	0.3 (s, 18H, CH$_3$, ^{t}Bu)
4	2141 (f), 2159 (sh)	−4.3 (s)	5.6 (s, 12H, C$_6$H$_6$) 0.3 (s, 18H, CH$_3$, ^{t}Bu)
5	2139 (f), 2156 (sh)	−5.4 (s br)	0.25 (s, 18H, CH$_3$, ^{t}Bu)

[a] In CH$_2$Cl$_2$. [b] In CD$_2$Cl$_2$.

methanide carbon atoms, giving several intermediates containing the diphosphine {(PPh$_2$)$_2$C(H)CN}, which is followed by rapid proton transfer processes from this cyanodiphosphine to the ruthenium complexes still containing the ligand {(PPh$_2$)$_2$CH}$^-$. The reaction mixture can be separated by a chromatography column. Unfortunately the characteristics of this reaction led to a low yield for derivative **2** (6%).

The new compounds **1** and **2** were characterized by spectroscopic methods (Table 1). The data confirmed the proposed structures. In both complexes, the IR spectrum showed only one ν_{CN} band, around 2140 cm^{-1}, instead of the expected two due to both types of CN groups present corresponding to the cyanodiphosphinomethanide and to the isocyanide ligand. This pattern can be attributed to the coincidence of the ν_{CN} value for both groups, as in the related compound [Mn(CO)$_3$(CN^{t}Bu)-{(PPh$_2$)$_2$CCN}].[5]

Compound **1** displayed an interesting pattern in its ^{31}P{^{1}H} NMR spectrum, being a second-order AA′BB′ spin system. The spin simulation parameters used for obtaining a best fit to the measured spectrum are listed in Table 1. The phosphorus NMR spectrum for complex **2** showed a singlet, and in the ^{1}H NMR spectrum no methylenic protons were observed. Both results are in accordance with the proposed formulation. The structure of **2** was confirmed by an X-ray diffraction study on a suitable crystal (Figure 1). The ruthenium atoms lie on an inversion center, so the complex cation is centrosymmetric. The coordination sphere around the metal center has a distorted octahedral geometry, as the equatorial angles need to accommodate to the requirement of the chelate rings. The CP$_2$RuP$_2$C skeleton is planar, and the CCN groups of the diphosphine ligands are linear. The bond distance between the two carbons (1.38(1) Å) in the CCN fragment is shorter than a single bond, which indicates that out of the two simple resonance forms that can describe the bond in this ligand (Figure 2), form **b** has some participation, although the CN bond length (1.16(1) Å) is similar to the one observed in free nitriles (1.158 Å in MeCN).[6] In fact, both distances are close to those usually found in related keteniminato compounds.[7]

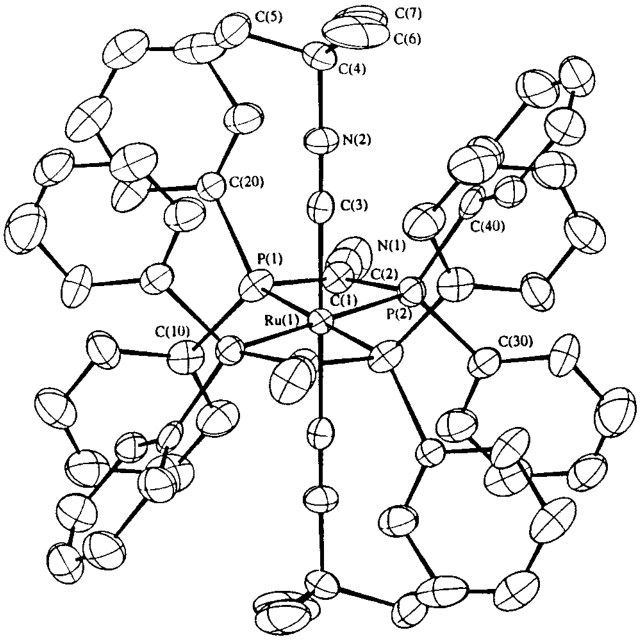

Figure 1. Molecular structure of **2** together with the atomic numbering system. Selected bond lengths (Å) and angles (deg): Ru(1)−P(1) 2.379(3), Ru(1)−P(2) 2.374(2), P(2)−C(1) 1.77(1), P(1)−C(1) 1.68(7), C(1)−C(2) 1.38(1), C(2)−N(1) 1.16(2), C(3)−N(2) 1.16(1), P(1)−C(1)−P(2) 100.9(9), C(1)−C(2)−N(1) 177.5(14), P(1)−C(1)−C(2) 128.3(12), P(2)−C(1)−C(2) 130.7(10).

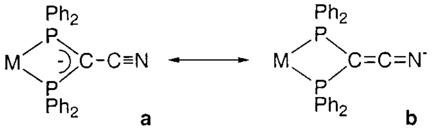

Figure 2.

The structure observed for {(PPh$_2$)$_2$CCN}$^-$ in **2** suggests an additional coordination ability in the ligand by either the methanide carbon or the nitrogen atom. It is then a promising substrate for the synthesis of heterometallic species. Hence we studied the reactivity of **2** toward the metallic substrates [AuCl(PPh$_3$)], [Cu(NCMe)$_4$](BF$_4$), and [RuCl$_2$(C$_6$H$_6$)(NCMe)]. As shown in Scheme 2 in these three cases the compound **2** behaved as a dinitrile, coordinating to the metallic fragments

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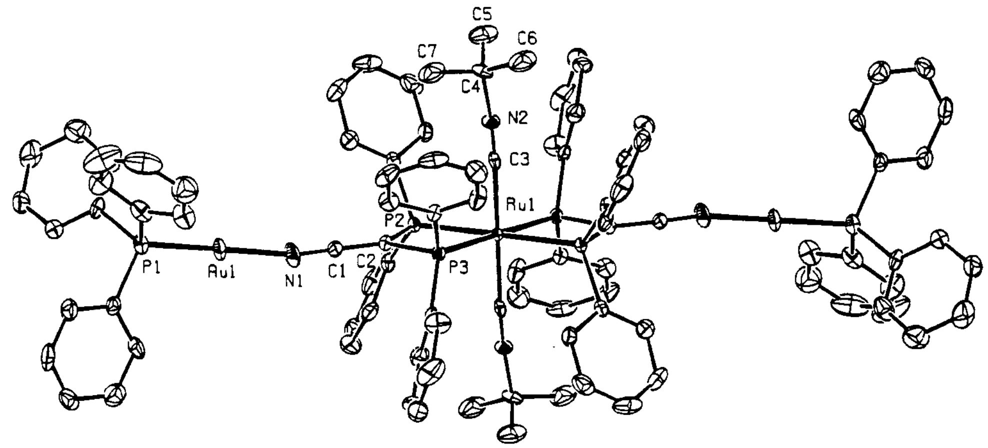
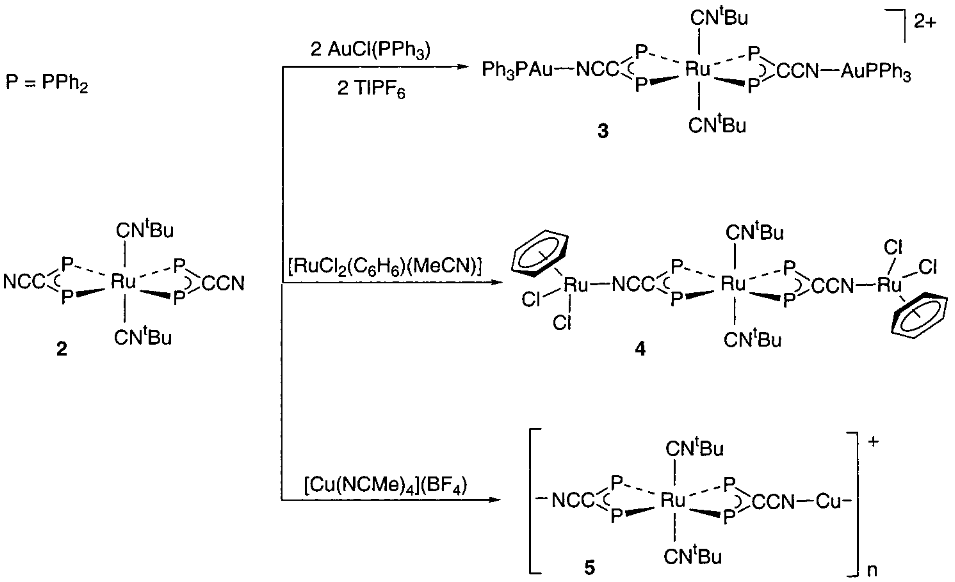


Figure 3. Molecular structure of the cationic complex in **3** together with the atomic numbering system. Selected bond lengths (Å) and angles (deg): Au(1)−N(1) 2.009(12), Au(1)−P(1) 2.230(4), P(2)−C(2) 1.783(13), P(3)−C(2) 1.760(13), C(1)−C(2) 1.364(18), C(1)−N(1) 1.159(17), C(3)−N(2) 1.113(15), Ru(1)−P(2) 2.372(3), Ru(1)−P(3) 2.393(3), Ru(1)−C(3) 2.050(15), C(1)−C(2)−P(2) 127.9(10), C(1)−C(2)−P(3) 130.2(11), P(3)−C(2)−P(2) 101.8(6), N(1)−C(1)−C(2) 178.5(16), C(1)−N(1)−Au(1) 166.8(13), N(1)−Au(1)−P(1) 174.9(4).

Scheme 2



through the nitrogen atoms, leading to the formation of the species *trans*-[Ru(CN^{t}Bu)$_2${(PPh$_2$)$_2$CCN−Au(PPh$_3$)}$_2$]$^{2+}$ (**3**), *trans*-[Ru(CN^{t}Bu)$_2$ {(PPh$_2$)$_2$CCN−RuCl$_2$(C$_6$H$_6$)}$_2$] (**4**), and *trans*-[Ru(CN^{t}Bu)$_2${(Ph$_2$P)$_2$CCN−Cu−NCC(Ph$_2$P)$_2$}]$_n^+$ (**5**), respectively. The substitution of Cl$^-$ in [AuCl(PPh$_3$)] by the cyanomethanide was facilitated by the presence of TlPF$_6$ as a halogen abstractor, whereas in the two other complexes the acetonitrile ligands were easily substituted by the metalloligand **2**.

In the IR spectra of **3**−**5** (Table 1) the ν_{CN} bands appeared at higher frequencies than those of **2**, especially the one corresponding to the cyanomethanide group, which is naturally strongly affected by the coordination to a new metallic center and hence appears as a shoulder around 2156 cm^{-1}. It should be noted that, as reported in the literature, the ν_{CN} bands of nitrile ligands usually shift to higher values when coordinated.[8]

In the ^{31}P{^{1}H} NMR spectra of **3**−**5** the signal corresponding to the PPh$_2$ groups was close to that observed in **2**. The proton NMR spectra displayed signals due to the hydrogens of Ph and ^{t}Bu groups presenting the right integral values. No bands for the MeCN groups were observed in **4** and **5**, corroborating the total substitution of this ligand by **2**.

Only in the case of **3** were suitable crystals for X-ray diffraction grown from the slow diffusion of a CH$_2$Cl$_2$ solution in diethyl ether (Figure 3). In this centrosymmetric cation the ruthenium appears in a quasi-octahedral environment. As in **2**, the CP$_2$RuP$_2$C skeleton is planar. Within the CCNAuP fragment the gold atom presents a linear coordination (N(1)−Au(1)−P(1) = 174.9(4)°). Equally the CCN group shows a linear disposition (C(2)−C(1)−N(1) = 178.5(16)°). The bond distances and angles in the skeleton P$_2$CCN are very similar to those of **2**, showing little influence of the coordination of the two [Au(PPh$_3$)]$^+$ units in the structural parameters of complex **3**. Finally, the value of the angle C(1)−N(1)−Au(1) (166.8 (13)°) is slightly smaller than the one more often observed in nitrile compounds (175 ± 5°). This shift from linear geometry could be attributed to an sp^2 contribution to the electronic state of the nitrogen atom, although the packing interactions could be as well responsible of this deviation, as an interaction between the gold atom of one molecule and the PPh_3 group of another surrounding molecule is observed in the packing arrangement.

The isolation of the polymeric species **5** shows the suitability of **2** for the synthesis of metal-containing polymers. The analytical and spectroscopic date for **5** are in accordance with the proposed formulation, which is also supported by the structural determination of the closely related trimetallic complex *fac*-[{Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CCN}}$_2$Cu](BF$_4$) carried out in a previous work of our group.[5] A relation can be found between **5** and the polymetallic transition metal compounds containing the cyanide ion and other π-ligands in their backbones, which possess a rich structural chemistry and show very interesting optical and electronic properties.[9] Unfortunately **5** was not stable enough to accomplish a deeper study of its structure and properties.

To conclude, we describe in this paper the syntheses of the complex *trans*-[Ru(CN^{t}Bu)$_2${(PPh$_2$)$_2$CCN}$_2$] (**2**), which behaves as a dinitrile metalloligand, allowing the synthesis of a variety of polymetallic species such as *trans*-[Ru(CN^{t}Bu)$_2${(PPh$_2$)$_2$CCN−Au(PPh$_3$)}$_2$]$^{2+}$ (**3**), *trans*-[Ru(CN^{t}Bu)$_2${(PPh$_2$)$_2$CCN−RuCl$_2$(C$_6$H$_6$)}$_2$] (**4**), and *trans*-[Ru(CN^{t}Bu)$_2${(Ph$_2$P)$_2$CCN−Cu−NCC(Ph$_2$P)$_2$}]$_n^+$ (**5**) when treated with the appropriate metallic fragment.

Experimental Section

General Considerations. For the general experimental procedure see ref 3c. The compounds *trans*-[Ru(CN^{t}Bu)$_2$(dppm)$_2$](PF$_6$)$_2$,[10] [Ru(Cl)$_2$(C$_6$H$_6$)(NCMe)],[11] [Cu(NCMe)$_4$](BF$_4$),[12] and [AuCl(PPh$_3$)][13] were prepared as described elsewhere.

***trans*-[Ru(CN^{t}Bu)$_2${(Ph$_2$P)$_2$CCN}$_2$] (2).** The compound *trans*-[Ru(CN^{t}Bu)$_2${(Ph$_2$P)$_2$CH}$_2$] was prepared in situ by the reaction of *trans*-[Ru(CN^{t}Bu)$_2$(dppm)$_2$](PF$_6$)$_2$ with KOH. Thus, to a solution of 0.3 g (0.23 mmol) of *trans*-[Ru(CN^{t}Bu)$_2$(dppm)$_2$](PF$_6$)$_2$ in 20 mL of CH_2Cl_2 was added 2.5 g of KOH and the resulting suspension obtained stirred for 2 h. Then the solution was filtered, and $(CN)_2$ was bubbled through the solution for 3 h. The solvent was taken off under vacuum and the remaining solid chromatographed through an alumina column (activity III). Elution with CH_2Cl_2/hexane (2:1) and evaporation of the solvent gave the desired product **2**. Yield: 15 mg (6%). Anal. Calcd for $RuP_4C_{62}H_{58}N_4$: C, 68.69; H, 5.39; N, 5.17. Found: C, 68.47; H, 5.22; N, 4.98.

The compound *trans*-[Ru(CN^{t}Bu)$_2$(dppm){(Ph$_2$P)$_2$CCN}](PF$_6$) (**1**) was eluted from the column with CH_2Cl_2 and isolated from the solution by the addition of hexane. Yield: 130 mg (48%). Anal. Calcd for $RuF_6P_5C_{61}H_{60}N_3$: C, 60.85; H, 5.01; N, 3.49. Found: C, 60.42; H, 4.85; N, 3.24. ^{1}H NMR (CDCl$_3$): δ 7.7−7.2 (40H, Ph); 5.2 [t, 2H, $^2J_{PH}$ = 8, CH_2]; 0.4 (s, 18H, CN^{t}Bu).

***trans*-[Ru(CN^{t}Bu)$_2${(Ph$_2$P)$_2$CCNAu(PPh$_3$)}$_2$](PF$_6$)$_2$ (3).** To a dichloromethane solution (10 mL) of **2** (25 mg, 0.02 mmol) were added 23 mg (0.04 mmol) of [AuCl(PPh$_3$)] and 32 mg (0.08 mmol) of TlPF$_6$. The reaction mixture was stirred for 2 h. The solution was then filtered and 15 mL of ether carefully added to the filtrate. Slow diffusion of the solvents afforded crystals of **3**. Yield: 35 mg (76%). Anal. Calcd for $RuAu_2F_{12}P_8C_{98}H_{88}N_4\cdot 2CH_2Cl_2$: C, 48.78; H, 3.77; N, 2.27. Found: C, 48.99; H, 3.80; N, 2.17.

***trans*-[Ru(CN^{t}Bu)$_2${(Ph$_2$P)$_2$CCN−Ru(Cl)$_2$(C$_6$H$_6$)}$_2$] (4).** To a solution of **2** (10 mg, 0.01 mmol) in 10 mL of CH_2Cl_2 was added 8 mg (0.03 mmol) of [Ru(Cl)$_2$(C$_6$H$_6$)(NCMe)]. The solution was stirred for 2 h. The solvent was eliminated to dryness and the resulting residue washed with ether, affording **4** as a dark green solid. Yield: 12 mg (82%). Anal. Calcd for $Ru_3Cl_4P_4C_{74}H_{70}N_4\cdot CH_2Cl_2$: C, 54.94; H, 4.26; N, 3.28. Found: C, 54.39; H, 4.48; N, 3.51.

***trans*-[Ru(CN^{t}Bu)$_2${(Ph$_2$P)$_2$CCN−Cu−NCC(Ph$_2$P)$_2$}]$_n$(BF$_4$)$_n$ (5).** A 10 mg sample of **2** (0.01 mmol) was dissolved in 7 mL of dichloromethane. To this solution was added 3 mg (0.01 mmol) of [Cu(NCMe)$_4$](BF$_4$). After 1 h of stirring the solvent was evaporated to dryness, affording the compound **5** as a white solid. Yield: 10 mg (81%). Anal. Calcd for $RuCuBF_4P_4C_{62}H_{58}N_4$: C, 60.32; H, 4.73; N, 4.54. Found: C, 60.43; H, 4.69; N, 4.08.

X-ray Crystallography. Crystal data for **2**: [$C_{62}H_{58}RuN_4P_4$]·$2CH_2Cl_2$, fw = 1254.00, monoclinic, space group *C*2/*m*, a = 12.011(3) Å, b = 23.027(6) Å, c = 12.60(1) Å, β = 116.93(5)°, V = 3107(5) Å^3, Z = 2, ρ_{calc} = 1.34 Mg m^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 5.62 cm^{-1}, T = 293 K, orange crystal (0.30 × 0.26 × 0.23 mm). Nonius CAD4 diffractometer; $\omega-2\theta$ scan technique; 2948 reflections measured (1° < θ < 25°), 2049 used in refinement, R(int) = 0.30. The structure was solved by Patterson methods using CRYSTALS[14] adapted on a Micro Vax II and refined by full-matrix least-squares on F^2 procedures: R = 0.044 and R_w = 0.049; total number of parameters 350; largest diff peak and hole 0.39 and −0.39 e Å^{-3}. The view of the molecule is done using Cameron.[15] Crystal data for **3**: $C_{100}H_{92}Au_2Cl_4F_{12}N_4P_8Ru$, fw = 2426.53, triclinic, space group $P\bar{1}$, a = 13.329(5) Å, b = 13.90(2) Å, c = 13.969(6) Å, α = 86.12(7)°, β = 81.26 (4)°, γ = 86.62(7)°, V = 2549(3) Å^3, Z = 1, ρ_{calc} = 1.634 Mg m^{-3}, F(000) = 1237.0, λ(Mo Kα) = 0.71073 Å, μ = 3.29 cm^{-1}, T = 200 K, white crystal (0.132 × 0.198 × 0.099 mm). Nonius CAD4 diffractometer; $\omega-2\theta$ scan technique; 8971 independent reflections measured (1.47° < θ < 24.98°), all used in refinement. The structure was solved by Patterson methods and phase expansion using DIRDIF[16] and refined by full-matrix least-squares on F^2 procedures: R = 0.0601 (for all reflections) and wR2 = 0.1655 (for all reflections), $w = 1.0/[\sigma^2(F_o)^2 + (0.1000P)^2 + 0.00P]$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$; total number of parameters 599; largest diff peak and hole 2.35 and −1.44 e Å^{-3}. The plot in Figure 3 was made by the EUCLID package.[17] Additional crystallographic data are available in the Supporting Information.

Acknowledgment. We gratefully acknowledge the Spanish Ministerio de Ciencia y Tecnología for financial assistance (Project BQU2000-0220) and for a research grant (M.E.G.M.).

Supporting Information Available: Tables of bond distances, angles, positional parameters, anisotropic thermal parameters, and hydrogen atom coordinates of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010243F

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