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Synthesis and Reactivity of Triruthenium Carbonyl Cluster Complexes Containing a Bridging 1-Azavinylidene Ligand Derived from Benzophenone Imine[†]

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The reaction of $[Ru_3(CO)_{12}]$ with the lithium salt of benzophenone imine ($LiN{=}CPh_2$) followed by protonation with trifluoroacetic acid leads to the η^1-1-azavinylidene cluster complex $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**). Compound **1** cannot be prepared by direct reaction of $[Ru_3(CO)_{12}]$ with benzophenone imine under thermal conditions. Carbonyl substitution and thermolysis reactions on compound **1** and on some of its derivatives are described. Complex **1** reacts with 1 and 2 equiv of bis(diphenylphosphino)methane (dppm) at room temperature to give the substituted derivatives $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-dppm})(CO)_8]$ (**2**) and $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-dppm})(dppm)(CO)_7]$ (**3**), respectively. In both complexes the three bridging ligands span the same Ru−Ru edge; in addition, complex **3** contains an η^1-dppm ligand occupying an equatorial site on the unique Ru atom. An X-ray structure analysis of $\mathbf{3}\cdot 0.5CH_2Cl_2$ is reported. Thermolysis of complex **2** in THF at reflux temperature leads to $[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(\mu\text{-dppm})(CO)_7]$ (**4**), a compound which contains a bridging η^2-1-azavinylidene ligand interacting with the three Ru atoms. Complex **4** reacts with CO (1 atm, 18 °C) reverting to complex **2**. The reaction of compound **1** with PPh_3 at room temperature gives the monosubstituted derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_3)(CO)_9]$ (**5**), in which the *P*-donor ligand is attached to one of the two bridged Ru atoms. Thermolysis of **5** in THF at reflux temperature leads to $[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(PPh_3)(CO)_8]$ (**6**), which, as complex **4**, contains a face-bridging η^2-1-azavinylidene ligand. The reaction of complex **5** with PPh_3 occurs only at higher temperatures (40−70 °C) to give the asymmetrically disubstituted derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_3)_2(CO)_8]$ (**7**), which has the additional PPh_3 ligand attached to the unbridged Ru atom. Compound **7** is thermally unstable, undergoing an easy (40−70 °C) orthometalation reaction of a phenyl ring of the azavinylidene ligand to give the derivative $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPhC_6H_4)(PPh_3)_2(CO)_7]$ (**8**). This compound reacts with CO (1 atm, 18 °C) to regenerate complex **7**.

Introduction

Most *N*-unsubstituted Schiff bases, $HN{=}CR^1R^2$, particularly those derived from all types of aldehydes or from ketones with alkyl R groups, are very unstable at room temperature. This low stability has been an impediment to the study of their behavior as ligands. In fact, in most cases, their metal complexes have been prepared by reactions that modify coordinated ligands (nitriles, oximes, azines, diazirines, diazepines, silyl- and stannylimines, imido ligands, etc.) instead of using *N*-unsubstituted imines as ligand precursors.[1,2]

Benzophenone imine has recently become commercially available, and this has allowed a considerable development of its inorganic chemistry. In mononuclear compounds, its coordination chemistry is represented by Mo,[3] W,[3] Fe,[4] Ru,[5] Os,[6−11] Rh,[2] Ir,[2,9] and Ni[12] complexes corresponding to the coordination types shown in Chart 1, which involve η^1-terminal ligands (**A**, **B**), η^2-terminal ligands (**C**), and orthometalated ligand derivatives (**D**, **E**). Binuclear complexes derived from this ligand have only been reported for Mo,[3] W,[3] Fe,[4] Rh,[2] and Ir[2] (**F**) (Chart 1).

[†] Dedicated to Professor Rafael Usón on his 70th birthday.

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Chart 1

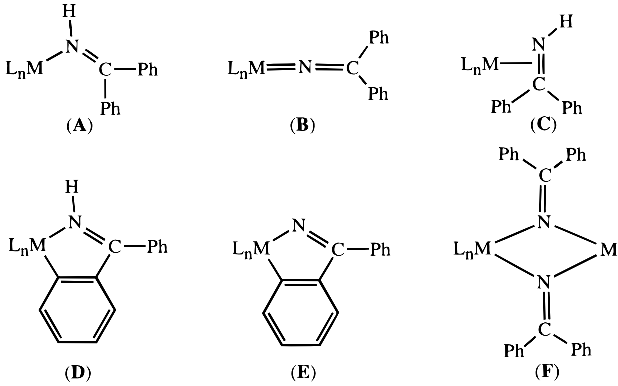
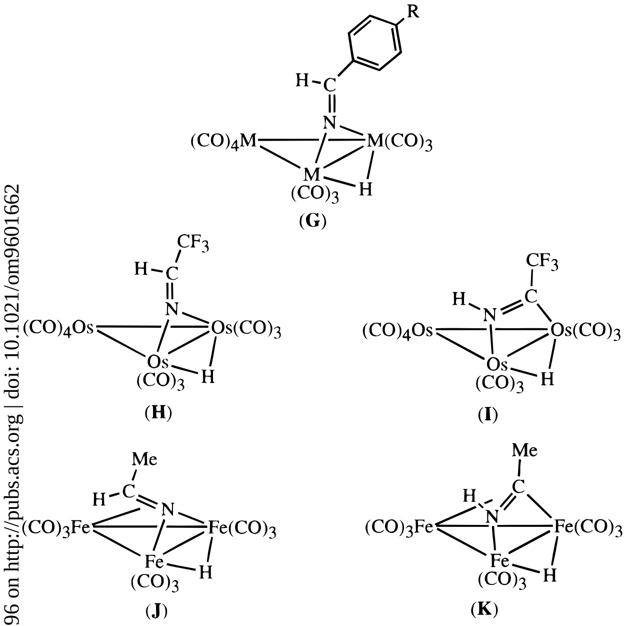
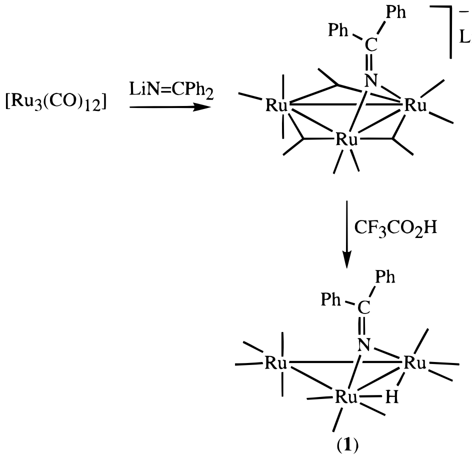


Chart 2



In the case of transition metal carbonyl cluster compounds, the only previous examples known to contain *N*-unsubstituted imine-type ligands are aldehyde imine derivatives.[13−21] Thus, compounds of type **G** (Chart 2) have been prepared in low yields by treating aromatic nitriles with $[M_3(CO)_{12}]$ (M = Ru, Os) in the presence of carboxylic acids or molecular hydrogen.[13−17] In a related reaction, insertion of trifluoroacetonitrile into an Os−H bond of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ gives the isomeric compounds **H** and **I** (Chart 2).[18−20] The isomeric face-bridged derivatives **J** and **K**, derived from the reduction of acetonitrile on iron clusters, have also been reported.[21]

Scheme 1



It should be noted that the *N*-donor ligands in compounds of types **B**, **F**−**H**, and **J** can be regarded as 1-azavinylidene or alkylideneimido ligands.

We now report the synthesis of a new triruthenium cluster, $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**), which contains an edge bridging η^1-1-azavinylidene ligand derived from benzophenone imine. The fact that compound **1** represents the first trinuclear transition metal cluster containing a 1-azavinylidene ligand with a disubstituted carbon atom, coupled to its air-stability and efficient preparation (67% isolated yield, based on the amount of starting $[Ru_3(CO)_{12}]$), led us to undertake a study of its reactivity. We also report here that carbonyl substitution and thermolysis reactions on compound **1** and on some of its derivatives have led not only to new cluster complexes containing μ-η^1-1-azavinylidene ligands but also to an orthometalated μ-η^2-1-azavinylidene derivative and to two trinuclear compounds containing a μ_3-η^2-1-azavinylidene ligand.

Results and Discussion

Synthesis of Compound 1. No reaction was observed between $[Ru_3(CO)_{12}]$ and benzophenone imine (THF or toluene, reflux temperature, 2 h). However, the lithium salt of benzophenone imine, $LiN{=}CPh_2$, reacted smoothly (THF, 18 °C, 2 h) with $[Ru_3(CO)_{12}]$ to give a very air-sensitive anionic derivative, $[Ru_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}CO)_3(CO)_7]^-$, which was not isolated. The structure proposed for this species in Scheme 1 is based on the similarity of its IR spectrum with those of the related anionic compounds $[Ru_3(\mu\text{-}dmpz)(\mu\text{-}CO)_3(CO)_7]^-$ (Hdmpz = 3,5-dimethylpyrazole)[22] and $[Ru_3(\mu\text{-}Opy)(\mu\text{-}CO)_3(CO)_7]^-$ (HOpy = 2-pyridone),[23] which also contain 3-electron donor ligands. The latter has been made by a synthetic procedure analogous to that of the 1-azavinylidene derivative and has been characterized by X-ray diffraction methods. Protonation of $[Ru_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}CO)_3(CO)_7]^-$ led to the neutral hydrido derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**), which was isolated as an orange, air-stable solid. Its most relevant IR and NMR data are collected in Tables 1−3. The symmetric structure (C_s) proposed for this compound in Scheme 1 is strongly supported by its $^{13}C\{^1H\}$ NMR spectrum (Table 3), which shows six carbonyl resonances of the

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Table 1. Selected IR Data

compd	ν(CO)/cm^{-1}
1^a	2100 (w), 2066 (vs), 2051 (s), 2023 (vs), 2011 (s), 2005 (s), 1990 (w)
2^b	2059 (s), 2006 (vs), 1994 (m), 1979 (s), 1943 (w)
3^b	2025 (m), 1991 (vs), 1974 (m), 1954 (vs), 1918 (w)
4^b	2038 (s), 2012 (vs), 1992 (w), 1970 (s), 1946 (w)
5^b	2081 (m), 2044 (s), 2009 (vs), 1984 (m), 1972 (w), 1956 (w)
6^b	2071 (m), 2035 (s), 2009 (vs), 1974 (m), 1948 (m)
7^c	2059 (m), 2019 (vs), 1989 (m), 1956 (m)
8^b	2071 (w), 2008 (vs), 1949 (m)

^{a} In hexane. ^{b} In THF. ^{c} In CH_2Cl_2.

Table 2. Selected ^{1}H and ^{31}P{^{1}H} NMR Data

compd	$\delta(\mu$-H)/ppm^a	δ(P)/ppm^a
1	−13.94 (s)	
2^b	−12.89 (t) [14.1]	10.16 (s)
3^c	−12.76 (t) [13.1]	30.17 (dt) {44.4, 17.0}, 9.85 (d, 2 P) {17.0}, −25.50 (d) {44.4}
4^d	−15.37 (t) [13.3]	32.15 (s)
5	−13.12 (d) [7.4]	30.97 (s)
6^e	−14.33 (d) [10.4]	37.10 (s)
7	−12.69 (dd) [5.5, 3.5]	37.32 (d) {31.2}, 28.61 (d) {31.2}
8	−10.81 (dd) [8.0, 4.1], −14.78 (dd) [12.1, 5.9]	32.42 (d) {29.7}, 31.41 (d) {29.7}

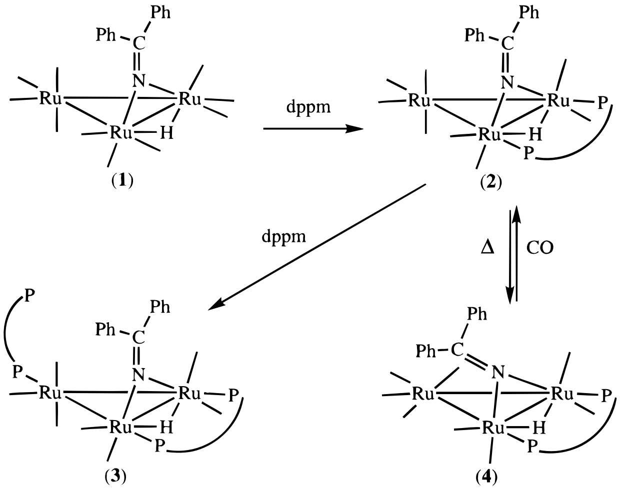
^{a} Spectra were recorded in $CDCl_3$; multiplicities are given in parentheses; coupling constants (Hz) are given in brackets [J(H−P)] or braces {J(P−P)}. ^{b} $\delta(CH_2)$ = 3.63 (m, 1 H), 2.93 (m, 1 H). ^{c} $\delta(CH_2)$ = 3.53 (m, 1 H), 2.72 (m, 1 H), 1.26 (t, J = 7.0 Hz, 1 H), 0.91 (t, J = 6.0 Hz, 1 H). ^{d} $\delta(CH_2)$ = 3.57 (m, 1 H), 2.62 (m, 1 H). ^{e} In CD_2Cl_2.

Table 3. Selected ^{13}C{^{1}H} NMR Data

compd	δ(CO)/ppm^a	δ(N=C)/ppm^a
1^b	207.7 (s), 204.8 (s), 201.8 (s, 2 C), 194.2 (s, 2 C), 193.8 (s, 2 C), 184.7 (s, 2 C)	182.4 (s)
2^c	210.3 (s, 2 C), 208.0 (m, 3 C), 199.5 (s, 3 C)	178.4 (s)
3^d	216.2 (m, 2 C), 210.0 (s, 3 C), 202.0 (s, 2 C)	175.8 (s)
4^e	205.0 (s, 3 C), 197.8 (m, 2 C), 195.2 (s, 2 C)	144.6 (s)
5^f	209.0 (s), 207.2 (d, 15.0), 206.9 (s), 202.9 (s), 197.3 (d, 5.1), 196.9 (s), 195.4 (d, 9.3), 194.3 (s), 188.3 (s)	178.1 (s)
6^g	201.5 (s), 199.4 (s), 197.0 (d, 5.0), 196.4 (s), 195.6 (d, 6.1), 194.4 (s), 193.5 (s), 184.8 (d, 9.2)	145.6 (s)
7^h	215.3 (s), 215.2 (s), 212.1 (s), 212.3 (s), 207.9 (d, 6.0), 202.0 (s), 201.9 (s), 199.4 (d, 2.0)	177.5 (s)
8^i	205.3 (d, 7.4), 203.5 (s), 201.9 (d, 7.9), 200.6 (d, 6.0), 200.3 (d, 4.7), 199.3 (s), 190.0 (s)	182.0 (s)

^{a}Spectra were recorded in CD_2Cl_2; multiplicities, J(C−P) coupling constants (in Hz), and number of equivalent carbon atoms (other than one) are given in parentheses. ^{b} Other signals: 147.1 (s, 2 C, C_{ipso} of N=CPh_2), 132.7−126.0 (10 C). ^{c} Other signals: 146.9 (s, 2 C, C_{ipso} of N=CPh_2), 137.7−127.0 (34 C), 25.7 (t, 18.0 Hz, CH_2 of dppm). ^{d} Other signals: 147.2 (s, 2 C, C_{ipso} of N=CPh_2), 139.4−127.6 (58 C), 35.0 (m, CH_2 of dppm), 23.7 (t, 17.6 Hz, CH_2 of dppm). ^{e} Other signals: 151.0 (s, 2 C, C_{ipso} of N=CPh_2), 132.8−126.1 (34 C), 27.9 (t, 22.0 Hz, CH_2 of dppm). ^{f} Spectrum run at 215 K; other signals: 148.6 (s, C_{ipso} of N=CPh), 145.1 (s, C_{ipso} of N=CPh), 135.2−127.2 (28 C). ^{g} Spectrum run at 200 K; other signals: 151.7 (s, C_{ipso} of N=CPh), 150.2 (s, C_{ipso} of N=CPh), 134.8−128.3 (28 C). ^{h} Other signals: 148.5 (s, C_{ipso} of N=CPh), 145.6 (s, C_{ipso} of N=CPh), 137.5−127.8 (46 C). ^{i} Other signals: 170.7 (s, Ru-C of C_6H_4), 160.7 (s, C_{ipso} of C_6H_4), 137.8 (s, C_{ipso} of N=CPh), 140.2 (s, CH of C_6H_4), 134.5−125.6 (42 C), 124.4 (s, CH of C_6H_4), 120.9 (s, CH of C_6H_4).

Scheme 2



expected intensities (1:1:2:2:2:2) accompanied by the resonances of the bridging 1-azavinylidene ligand. The structure of complex **1** also supports the structure proposed for its anionic precursor $[Ru_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}CO)_3(CO)_7]^-$.

Kaesz was the first to report that the attack of $[Ru_3(CO)_{12}]$ by anionic nucleophiles X^- (amido groups, halides, etc.) results in the formation of anionic derivatives $[Ru_3(\mu\text{-}X)(CO)_{10}]^-$ that can be subsequently protonated to give $[Ru_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$.[24] We have recently reported that protonation of the anionic cluster $[Ru_3(\mu\text{-}dmpz)(\mu\text{-}CO)_3(CO)_7]^-$ leads to the neutral cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(CO)_{10}]$, a compound which, as occurs with compound **1**, cannot be prepared by direct reaction of $[Ru_3(CO)_{12}]$ with the neutral *N*-donor ligand precursor and which is structurally analogous to compound **1**.[22] Interestingly, the most convenient route to the anionic cluster $[Ru_3(\mu\text{-}dmpz)(\mu\text{-}CO)_3(CO)_7]^-$ is to treat $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ with 3,5-dimethylpyrazole,[22] while the anionic 1-azavinylidene derivative $[Ru_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}CO)_3(CO)_7]^-$ is best prepared from $[Ru_3(CO)_{12}]$ and the lithium salt of the bridging ligand (*vide supra*).

Some other ruthenium clusters containing bridging 1-azavinylidene ligands have been reported. They correspond to the general formula $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CHR)(CO)_{10}]$ and are isostructural with complex **1**, but they all contain a hydrogen atom on the azavinylidene carbon atom and have been made *via* hydrogenation reactions of coordinated nitrile ligands.[13−17] The structures of all these triruthenium clusters derived from *N*-unsubstituted Schiff bases are quite different from those found for clusters derived from *N*-substituted Schiff bases, in which both the N and C imine atoms are coordinated to the metals, as in compounds of types **I** and **K** (Chart 2).[25]

Complexes Derived from Compound 1 and Bis(diphenylphosphino)methane. The room-temperature reaction of complex **1** with 1 equiv of bis(diphenylphosphino)methane (dppm) in THF led to the disubstituted derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}dppm)(CO)_8]$ (**2**), which was isolated in 85% yield. Its ^{31}P{^{1}H} NMR spectrum contains only one singlet, while its ^{1}H NMR proton spectrum shows the hydride resonance as a triplet (Table 2), indicating that the three bridging ligands span the same Ru−Ru edge (C_s symmetry), as depicted in Scheme 2.

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[24] See, for example: (a) Szostak, S.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243. (b) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704. (c) Kampe, C. E.; Boag, N. M.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390. (d) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4640. (e) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647. (f) Boag, N. M.; Sieber, W. J.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1988**, *355*, 385.

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The mild conditions required for the formation of compound **2** and the isolation of only one of the possible isomers confirm that the 1-azavinylidene ligand has a strong *cis*-labilization effect.[26] Such a effect has been previously observed in other ruthenium carbonyl clusters containing bridging amido ligands,[27−30] but recent kinetic studies on carbonyl substitution reactions in edge-bridged triruthenium carbonyl cluster complexes have pointed out that the mechanism governing the *cis*-substitution (associative)[31] is different from that operating in mononuclear complexes (dissociative).[26]

The bis(dppm) derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}dppm)(dppm)(CO)_7]$ (**3**) was obtained in 92% yield when 2 equiv of dppm was allowed to react with complex **1**. Although the incorporation of two dppm ligands into the cluster was clearly evidenced by its analytical and spectroscopic data, its ^1H, ^{31}P, and ^{13}C NMR spectra at room temperature were deceptively simple, preventing a convincing structural assignment. Thus, the hydride ligand was observed as a triplet in the ^1H NMR spectrum (Table 2), three (and not four) resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum (a doublet at −25.5 ppm indicated of the presence of a monocoordinated dppm ligand), and only three (and not seven) carbonyl resonances were observed in the $^{13}C\{^1H\}$ NMR spectrum (Table 3). Lower temperature NMR measurements resulted in complex spectral changes, indicating that the simplicity of the room-temperature spectra is due to fluxional processes. It is accepted that phosphine substitution in carbonyl cluster compounds generally results in a slowing down of the carbonyl fluxionality as compared with that of their unsubstituted precursors,[30,32] but complex **1** proved to be stereochemically rigid at room temperature (*vide supra*), whereas the ligands of the substituted derivative **3** seem to be quite mobile.

The structure depicted in Scheme 2 for compound **3** is based on an X-ray diffraction analysis. Figure 1 shows the atomic labeling scheme. A selection of bond distances and angles is given in Table 4. The cluster consists of an isosceles triangle of ruthenium atoms with the shortest edge, Ru(1)−Ru(2), triply bridged by the hydride, 1-azavinylidene, and dppm ligands. A monocoordinated dppm ligand is attached to the unique Ru(3) atom in an equatorial position. The cluster shell is completed by seven terminal CO ligands. While the phosphorus atoms of the bridging dppm ligand are almost coplanar with the metal triangle (dihedral angle between the Ru_3 and Ru(1)−Ru(2)−P(1)−P(2) planes 9.4°), the hydride and 1-azavinylidene ligands are located to either sides of the Ru_3 plane (dihedral angles between this plane and the Ru(1)−Ru(2)−H(1) and Ru(1)−Ru(2)−N(1) planes −75.1 and 75.7°, respectively). The azavinylidene N(1)−C(9) bond distance, 1.28(2) Å, is consistent with a N=C double bond,[2] and the Ru(1), Ru(2), N(1), C(9), C(60), and C(70) atoms are almost coplanar. The structural features of the 2,2-diphenyl-1-azavinylidene ligand of complex **3** are comparable to those found in other binuclear[3,4,33−36] or trinuclear[13−20] complexes containing edge-bridging 2-*H*-1-azavinylidene ligands.

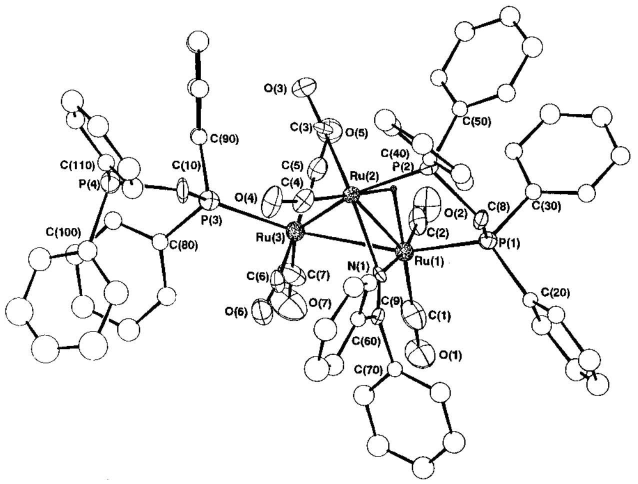

Figure 1. Structural plot of $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}dppm)(dppm)(CO)_7]$ (**3**) in $\mathbf{3}{\cdot}0.5CH_2Cl_2$. Thermal ellipsoids are drawn at the 30% probability level.

Table 4. Selected Bond Lengths and Bond Angles in $\mathbf{3{\cdot}0.5CH_2Cl_2}$

	Bond Lengths (Å)		
Ru(1)−Ru(2)	2.772(2)	Ru(1)−Ru(3)	2.838(2)
Ru(2)−Ru(3)	2.827(2)	Ru(1)−N(1)	2.05(1)
Ru(2)−N(1)	2.11(1)	Ru(1)−P(1)	2.352(5)
Ru(2)−P(2)	2.342(4)	Ru(3)−P(3)	2.318(5)
Ru(1)−C(1)	1.81(2)	Ru(1)−C(2)	1.83(2)
Ru(2)−C(3)	1.86(2)	Ru(2)−C(4)	1.84(2)
Ru(3)−C(5)	1.89(2)	Ru(3)−C(6)	1.86(2)
Ru(3)−C(7)	1.79(2)	Ru(1)−H(1)	1.72(4)
Ru(2)−H(1)	1.70(5)	P(1)−C(8)	1.82(2)
P(2)−C(8)	1.87(2)	P(3)−C(10)	1.81(2)
P(4)−C(10)	1.87(2)	N(1)−C(9)	1.28(2)
	Bond Angles (deg)		
Ru(1)−Ru(2)−Ru(3)	60.92(5)	Ru(1)−Ru(3)−Ru(2)	58.59(5)
Ru(2)−Ru(1)−Ru(3)	60.49(5)	Ru(1)−Ru(3)−P(3)	169.0(1)
Ru(3)−Ru(1)−P(1)	154.7(1)	Ru(3)−Ru(2)−P(2)	151.5(1)
Ru(2)−Ru(1)−C(1)	146.3(6)	N(1)−Ru(1)−C(2)	169.3(7)
N(1)−Ru(2)−C(3)	166.6(6)	Ru(1)−Ru(2)−C(4)	143.6(5)
C(5)−Ru(3)−C(6)	163.6(8)	Ru(2)−Ru(3)−C(7)	149.1(7)
Ru(1)−N(1)−Ru(2)	83.7(5)	Ru(1)−N(1)−C(9)	138.0(11)
Ru(2)−N(1)−C(9)	138.0(11)	C(60)−C(9)−C(70)	113.6(13)

The known iron complex $[Fe_3(\mu\text{-}H)(\mu_3\text{-}N{=}CHMe)(CO)_9]$ (**J** in Chart 1) contains a face-bridging 1-azavinylidene ligand.[21] Such a coordination mode for 1-azavinylidene ligands had no precedents in ruthenium chemistry. This led us to investigate the thermolysis reactions of compounds **1**−**3**.

No reaction was observed when complex **1** was stirred in THF or 1,2-dichloroethane at reflux temperature for 24 h. However, IR monitoring of a refluxing solution of compound **2** in THF showed that, after 1 h, the starting material was completely transformed into a new compound which was formulated as the face-bridged derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(\mu\text{-}dppm)(CO)_7]$ (**4**) on the basis of its analytical and spectroscopic data (Scheme 2). Only terminal CO ligands were observed

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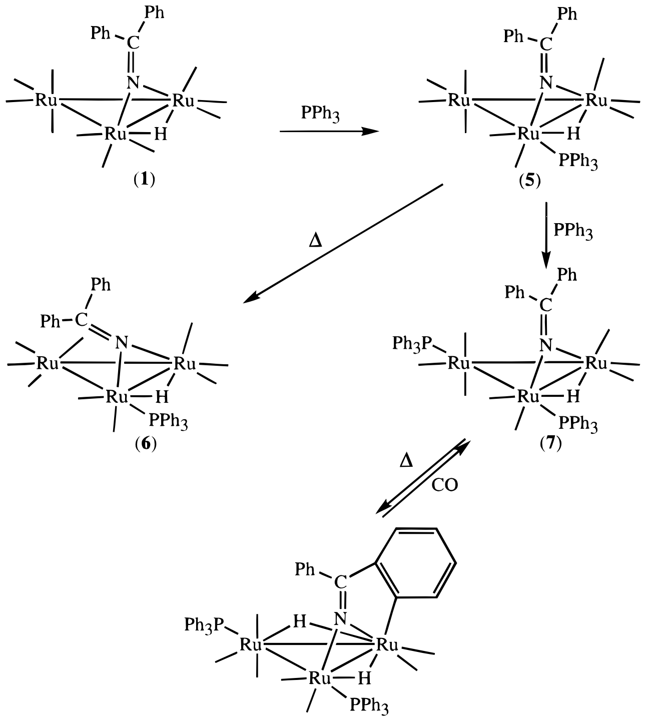
in its IR spectrum (Table 1). The ^{1}H, ^{31}P, and ^{13}C NMR spectra indicated that the structure of the compound is closely related to that of its precursor **2**, having the three bridging ligands spanning the same Ru−Ru edge. Thus, the proton spectrum shows the resonances of all the organic ligands and a triplet for the hydride ligand with a J(H−P) coupling constant very similar to those found for compounds **2** and **3** (Table 2), while the $^{31}P\{^{1}H\}$ NMR spectrum consists of only one singlet. Its $^{13}C\{^{1}H\}$ NMR spectrum (Table 3) was more informative since, although only three CO resonances of intensities 3:2:2 were observed (four CO resonances of intensities 1:2:2:2 are expected for the structure depicted in Scheme 2), the resonance of the azavinylidene carbon atom was observed at 144.6 ppm, shifted 31−37 ppm to lower frequencies from the N═*C* resonances of all the edge-bridged compounds described in this article. These data strongly support that the 1-azavinylidene ligand in complex **4** is behaving as a face bridging ligand, with the C═N double bond coordinated to the unique ruthenium atom, as shown in Scheme 2. This structural assignment is also supported by the fact that complex **4** reacted readily with carbon monoxide (1 atm, THF, 18 °C, 1 h) to give its octacarbonyl precursor **2**. We were unable to grow single crystals of compound **4**, and therefore, we could not confirm its structure by diffraction methods. As far as we know, this type of coordination for 1-azavinylidene ligands has only been reported for the iron cluster [$Fe_3(\mu\text{-}H)(\mu_3\text{-}N{=}CHMe)(CO)_9$].[21] Ruthenium cluster complexes containing μ_3-vinylidene ligands are also scarce,[37] although more examples are known for triiron carbonyl clusters.[38]

Thermolysis of compound **3** was expected to result in a release of CO accompanied by coordination of either the free phophorus atom or the C═N moiety of the azavinylidene ligand. However, no transformation was observed when compound **3** was stirred in THF at reflux temperature for 2.5 h. This result indicates that the CO ligands of heptacarbonyl derivatives of the triruthenium 1-azavinylidene system have no tendency to be replaced by other ligands.

Complexes Derived from Compound 1 and Triphenylphosphine. Triphenylphosphine is a monodentate ligand and is less basic than dppm. In addition, the stereochemistry of bis(triphenylphosphine) trinuclear clusters[29] is in most cases different from that of μ-η^2-dppm trinuclear derivatives,[27] in which the rigidity of the bidentate ligand forces the phosphorus atoms to be coordinated to adjacent metal atoms in neighboring positions (Scheme 2). Therefore, we decided to prepare triphenylphosphine derivatives of compound **1**, expecting that they would exhibit new reactivity and structural attributes.

The room-temperature reaction of compound **1** with 1 equiv of triphenylphosphine (THF, 72 h) led to the monosubstituted derivative [$Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_3)(CO)_9$] (**5**). The use of an excess of phosphine ligand reduced the reaction time without formation of disubstituted products as long as the temperature was not increased. The position of the phosphine ligand in cluster **5** (Scheme 3) was inferred from its ^{1}H NMR spectrum (Table 2), which shows the hydride as a doublet with a J(H−P) coupling constant of 7.4 Hz. This value is within the range expected for *cis* arrangements of phosphine and hydride ligands in trinuclear clusters.[27−29]

Scheme 3



The thermolysis of complex **5** in refluxing THF led to a mixture whose composition varied with the reaction time. Monitoring of the reaction by IR and NMR spectroscopies indicated that the face-bridged derivative [$Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(PPh_3)(CO)_8$] (**6**) was the first product formed, but before all **5** was consumed, it started to decompose progressively into a mixture of the bis(phosphine) orthometalated derivative [$Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPhC_6H_4)(PPh_3)_2(CO)_7$] (**8**), an as yet unidentified compound which contains no hydride and no phosphine ligands (hereafter named **X**), and some other products in very small amounts. Thus, for example, a roughly 1:5:1:1 mixture of **5**, **6**, **8**, and **X** was obtained after 12 h of reaction (NMR integration). Unfortunately, all attempts to separate the mixtures by chromatographic means induced the decomposition of complexes **6** and **X** on the chromatographic supports (silica or alumina) and only **5** and **8** could be eluted and separated. Although we could not get complex **6** in a pure form, we managed to get most of its IR (Table 1) and NMR (Tables 2 and 3) data from the spectra of mixtures obtained at different reaction times. The structure proposed for this compound in Scheme 3 is based on these data. As occurs in complex **4**, the ^{13}C NMR resonance of the N═*C* carbon atom is observed at low frequency, 145.6 ppm, indicating that the 1-azavinylidene ligand occupies a face-bridging position in the cluster. Eight CO resonances are also observed in the ^{13}C NMR spectrum (Table 3). The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra also confirm the presence of a hydride and a phosphine ligands in a *cis* arrangement (J(H−P) = 10.4 Hz).[28,29]

The reaction of complex **1** with 2 equiv of triphen-

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ylphosphine in dichloromethane at reflux temperature for 12 h (only **5** is formed at room temperature) led to a mixture of two compounds, subsequently identified as $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_3)_2(CO)_8]$ (**7**) and $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPhC_6H_4)(PPh_3)_2(CO)_7]$ (**8**). Shorter reaction times resulted in mixtures of compounds **5**, **7**, and **8**; the shorter the time the more **5** and the less **8** were observed by IR and NMR spectroscopies, whereas longer reactions times or higher temperatures resulted in more **8**, less **7**, and none of **5**. Complex **8** was quantitatively prepared by treating **1** with 2 equiv of triphenylphosphine in THF at reflux temperature for 4 h. All attempts to separate complex **7** from its mixtures with **5** and **8** by chromatographic methods failed, since **7** was transformed into compound **8** on the chromatographic supports (silica or alumina). However, we did obtain pure complex **7** by treating **8** with carbon monoxide (1 atm, CH_2Cl_2, 18 °C, 30 min).

The structures proposed for compounds **7** and **8** in Scheme 3 are based on analytical and spectroscopic data. Both gave satisfactory CHN analyses and the corresponding molecular ions in their respective mass spectra. Their $^{31}P\{^1H\}$ NMR spectra consist of two doublets with large coupling constants (Table 2), indicating that the two phosphine ligands occupy equatorial positions on different metal atoms, being collinear with a metal−metal bond.[29] The ^1H NMR spectrum of compound **7** shows the hydride as a doublet of doublets (Table 2), with the largest J(H−P) coupling constant, 5.5 Hz, suggesting a *cis*-hydride−phosphine arrangement,[28,29] while the small value of the other coupling constant indicates that the hydride is far away from the other phosphine ligand. These data are conclusive as far as the position of the ligands in cluster **7** is concerned (Scheme 3). The ^1H NMR spectrum of compound **8** shows two hydride resonances, both as doublets of doublets, with J(H−P) coupling constants (Table 2) which indicate that both hydrides are *cis* to one phosphine and far away from the other phosphine. The presence of two hydride ligands in the cluster is consistent with the observation of an orthometalated phenyl ring in the DEPT ^{13}C NMR spectra of the complex, which show the resonances of that ring spread over the range 170−120 ppm (Table 3). The fact that all these resonances are singlets confirms that (a) the orthometalated ring does not belong to the phosphine ligands but to the azavinylidene ligand (this is also suggested by the $^{31}P\{^1H\}$ NMR spectrum, which is very similar to that of complex **7**) and (b) the metalation has taken place onto the ruthenium atom which is not attached to any of the phosphine ligands. Moreover, the hydride ligand which comes from the metalated ring is expected to occupy a bridging position *cis* to the metalated carbon atom, as shown in Scheme 3.

As far as we know, compound **8** is the first complex to contain an orthometalated 1-azavinylidene ligand bridging two metal atoms. Although the orthometalation of benzophenone imine has been previously reported for mononuclear complexes of ruthenium[5] and osmium,[6−11] to give metallacycles of type **D** (Chart 1), the ligand in these compounds cannot be considered as an azavinylidene.

Although $[Ru_3(CO)_{12}]$ is an exception, it is generally accepted that the more CO ligands that a triruthenium carbonyl cluster complex possesses, the easier is the substitution of a single CO ligand by other ligands. However, compound **1** is stable at high temperatures (50−100 °C), whereas the substituted compounds **2**, **5**, and **7** release CO on heating, promoting the coordination of the C═N moiety of the azavinylidene ligand (case of **2** and **5**) or the C−H activation of one of the phenyl rings (case of **7**). We have found no answers that could explain this behavior. It is also intriguing why, in the case of complex **7**, C−H activation is preferred over C═N coordination.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) 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) and by spot thin-layer chromatography (TLC). All reagents and TLC plates were used as received from Aldrich. Infrared spectra (Table 1) were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H (Table 2), $^{31}P\{^1H\}$ (Table 2), and $^{13}C\{^1H\}$ (Table 3) NMR spectra were run at 18 °C with Bruker AC-200 and AC-300 instruments, using $SiMe_4$ (internal, for ^1H and ^{13}C) or 85% H_3PO_4 (external, for ^{31}P) as standards ($\delta = 0$ ppm). Fast atom bombardment mass spectra were obtained on a Finningan Mat-95 spectrometer, using nitrobenzyl alcohol as matrix and cesium as bombarding gas. Microanalyses were obtained from the University of Oviedo Analytical Service.

$[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (1). A 1.6 M solution of BuLi in hexane (3.23 mL, 5.168 mmol) was injected into a solution of benzophenone imine (0.867 mL, 5.156 mmol) in THF (50 mL). After the solution was stirred for 45 min, $[Ru_3(CO)_{12}]$ (3.0 g, 4.695 mmol) was added. The resulting solution was stirred until all ruthenium carbonyl had reacted (disappearance of the strong 2060 cm^{-1} band and appearance of new $\nu(\mu\text{-}CO)$ bands at 1781 and 1774 cm^{-1} in the IR spectrum of the solution, *ca.* 2 h), being then treated with trifluoroacetic acid (1 mL). The solvent was removed under reduced pressure, and the residue was separated by column chromatography (neutral alumina, activity I, 25 × 2 cm). Hexane eluted some $[Ru_3(CO)_{12}]$. Hexane−dichloromethane (1:1) eluted complex **1**, which was obtained as an orange solid (2.300 g, 67%). Anal. Calcd for $C_{23}H_{11}NO_{10}Ru_3$: C, 36.13; H, 1.45; N, 1.83. Found: C, 36.49; H, 1.68; N, 1.71. MS (*m/e*): 764 (M^+).

$[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}dppm)(CO)_8]$ (2). A solution of compound **1** (50 mg, 0.065 mmol) and dppm (25.1 mg, 0.065 mmol) in THF (20 mL) was stirred for 24 h. The solvent was removed under reduced pressure and the residue chromatographed on a column of neutral alumina (activity I, 10 × 2 cm). Hexane−toluene (1:1) eluted complex **2**, which was obtained as a red solid (60 mg, 85%). Anal. Calcd for $C_{46}H_{33}NO_8P_2Ru_3$: C, 50.55; H, 3.04; N, 1.28. Found: C, 50.63; H, 2.97; N, 1.13. MS (*m/e*): 1095 ($M^+ + 2$).

$[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}dppm)(dppm)(CO)_7]$ (3). A solution of compound **1** (200 mg, 0.260 mmol) and dppm (200 mg, 0.520 mmol) in THF (20 mL) was stirred for 12 h. The color changed from orange to dark red. The solvent was removed under reduced pressure and the residue chromatographed on a column of neutral alumina (activity I, 10 × 2 cm). Dichloromethane eluted complex **3**, which was obtained as a red solid (350 mg, 92%). Anal. Calcd for $C_{70}H_{55}NO_7P_4Ru_3$: C, 58.01; H, 3.83; N, 0.97. Found: C, 57.69; H, 3.97; N, 0.89. MS (*m/e*): 1451 ($M^+ + 2$).

$[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(\mu\text{-}dppm)(CO)_7]$ (4). A solution of compound **1** (50 mg, 0.065 mmol) and dppm (25.1 mg, 0.065 mmol) in THF (20 mL) was stirred at reflux temperature for 1 h. The solvent was removed under reduced pressure and the residue washed with hexane (3 × 5 mL) to give complex **2** as an orange solid (64 mg, 93%). Anal. Calcd for $C_{45}H_{33}NO_7P_2$-

Ru_3: C, 50.75; H, 3.12; N, 1.32. Found: C, 50.61; H, 3.40; N, 1.21. MS (*m/e*): 1037 ($M^+ - CO$).

Reaction of Compound 4 with Carbon Monoxide. Carbon monoxide was bubbled through a solution of compound **4** (20 mg, 0.019 mmol) in THF (10 mL) for 1 h. The color changed from orange to red. An IR spectrum of the resulting solution indicated the complete transformation of compound **4** into compound **2**.

[Ru_3(*μ*-H)(*μ*-N=CPh_2)(PPh_3)$(CO)_9$] (5). Triphenylphosphine (17.1 mg, 0.065 mmol) was added to a solution of compound **1** (50 mg, 0.065 mmol) in THF (20 mL). After the solution was stirred for 72 h, the solvent was removed under reduced pressure and the residue chromatographed on a column of neutral alumina (activity I, 10 × 2 cm). Hexane–toluene (1:1) eluted complex **5**, which was obtained as an orange solid (33 mg, 51%). Anal. Calcd for $C_{40}H_{26}NO_9PRu_3$: C, 48.10; H, 2.62; N, 1.40. Found: C, 48.39; H, 2.80; N, 1.44. MS (*m/e*): 999 (M^+).

[Ru_3(*μ*-H)(μ_3-N=CPh_2)(PPh_3)$(CO)_8$] (6). A solution of complex **5** (100 mg, 0.100 mmol) in THF (20 mL) was stirred at reflux temperature for 12 h. The solvent was removed under reduced pressure, and the residue was analyzed by IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, which indicated a 1:5:1:1 mixture of compounds **5**, **6**, **8**, and **X**, respectively (see the Results and Discussion section). All attempts to separate compound **6** from the mixtures by chromatographic methods were unsuccessful, since it decomposed on the supports (silica or alumina) and could not be eluted.

Reaction of Compound 1 with 2 equiv of PPh_3. Triphenylphosphine (34.3 mg, 0.131 mmol) was added to a solution of compound **1** (50 mg, 0.065 mmol) in dichloromethane (20 mL). After the solution was stirred at reflux temperature for 12 h, the solvent was removed under reduced pressure. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue indicated a 5:1 mixture of compounds **7** and **8** accompanied by very small amounts of two other unidentified products. All attempts to isolate complex **7** free of impurities by this method were unsuccessful, since it was readily converted into compound **8** on the supports used for chromatographic separations (silica, alumina).

[Ru_3(*μ*-H)(*μ*-N=CPh_2)$(PPh_3)_2$$(CO)_8$] (7). Carbon monoxide was bubbled through a dichloromethane (10 mL) solution of compound **8** (50 mg, 0.042 mmol) for 30 min. The color changed from orange to red. The solvent was removed under reduced pressure, and the solid residue was washed with pentane to give compound **7** as a red solid (45 mg, 88%). Anal. Calcd for $C_{57}H_{41}NO_8P_2Ru_3$: C, 55.52; H, 3.35; N, 1.14. Found: C, 55.48; H, 3.51; N, 1.04. MS (*m/e*): 1233 (M^+).

[Ru_3(*μ*-H)$_2$(*μ*-N=$CPhC_6H_4$)$(PPh_3)_2$$(CO)_7$] (8). A solution of compound **1** (50 mg, 0.065 mmol) and triphenylphosphine (43.3 mg, 0.131 mmol) in THF (10 mL) was stirred at reflux temperature for 4 h. The color changed from red to orange. The solvent was removed under reduced pressure, and the oily residue was separated by column chromatography (neutral alumina, activiy I, 15 × 2 cm). Elution with hexane–toluene (1:1) afforded compound **8**, which was obtained as a yellow-orange solid (75 mg, 96%). Anal. Calcd for $C_{56}H_{41}NO_7P_2Ru_3$: C, 55.81; H, 3.43; N, 1.16. Found: C, 55.90; H, 3.50; N, 1.09. MS (*m/e*): 1205 (M^+).

Crystal Structure of Complex 3·0.5CH_2Cl_2. A red, parallelepipedal crystal of the solvate **3**·0.5CH_2Cl_2, grown by layering pentane on a solution of **3** in dichloromethane, at −20 °C, was used for the X-ray analysis. Selected crystallographic and refinement data are collected in Table 5. Unit cell dimensions were determined from the angular settings of 25 well-centered reflections. The space group was proposed after structure determination. Two standard reflections were monitored periodically, showing no change during data collection. Corrections for Lorentz and polarization effects were made. An absorption correction was applied using the program DIFABS[39] from CRYSTALS.[40] No extinction correction was necessary.

Table 5. Crystallographic and Refinement Data for 3·0.5CH_2Cl_2

formula	$C_{70}H_{55}NO_7P_4Ru_3{\cdot}0.5CH_2Cl_2$
fw	1491.78
cryst syst	triclinic
space group	$P\bar{1}$
a,b,c, Å	12.284(4), 13.551(4), 20.895(8)
α,β,γ, deg	75.14(3), 86.58(3), 82.44(3)
V, Å^3	3331(6)
Z	2
D_{calcd}, g/cm^3	1.49
μ, cm^{-1}	8.44
min, max corr factors	0.78, 1.18
cryst size, mm	0.55 × 0.40 × 0.35
radiation (λ, Å)	Mo Kα (0.7107)
diffractometer	Enraf-Nonius CAD4
monochromator	graphite
temp, K	293(2)
scan method	$\omega-2\theta$
scan range, deg	$0.8 + 0.345 \tan\theta$
h,k,l range	−11 to 11, −12 to 13, 0 to 20
θ range, deg	1−20
no. of rflns collctd	6422
no. of indep rflns	6192
$R_{int} = \Sigma(I - \langle I\rangle)/\Sigma I$	0.058
no. of rflns with $F_o^2 > 3\sigma(F_o^2)$	3796
no. of params	480
R^a	0.058
R_w^b	0.069
Δ/σ	0.1
max, min $\Delta\rho$, e/Å^3	1.06, −0.80

[a] $R = \Sigma|F_o - |F_c||/\Sigma F_o$. [b] $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, unit weights.

The structure was solved by direct methods and subsequent Fourier maps. Non-hydrogen atoms, except the carbon atoms of the phenyl groups and the atoms of the CH_2Cl_2 solvent molecule, were refined anisotropically. Only a few hydrogen atoms were found on difference maps, so they all were placed riding on their parent atoms with an overall isotropic thermal parameter, except the bridging hydrogen atom H(1), which was found and its positional and thermal parameters were refined isotropically. Refinements were carried out in three blocks by minimizing the function $\Sigma w(F_o - |F_c|)^2$. All calculations were performed with CRYSTALS.[40] Scattering factors were taken from the appropriate reference[41] and were corrected for anomalous dispersion. The structure plot in Figure 1 was carried out with the CAMERON package.[42] Selected interatomic distances and angles are given in Table 4.

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Supporting Information Available: Tables of atomic coordinates and *U* values, bond distances and angles, anisotropic thermal parameters, and H coordinates and *U* values for **3**·0.5CH_2Cl_2 (7 pages). Ordering information is given on any current masthead page.

OM9601662

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