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Approaches to Triosmium Carbonyl Cluster Compounds Derived from Benzophenone Imine. Characterization of Terminal Imino, Bridging Amido, and Orthometalated Imino Derivatives

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Summary: The cluster complexes $[Os_3H(\mu\text{-}H)(HN{=}CPh_2)(CO)_{10}]$ (**1**), $[Os_3(\mu\text{-}H)(\mu\text{-}HN{-}CHPh_2)(CO)_{10}]$ (**2**), $[Os_3(\mu\text{-}H)(\mu\text{-}HN{-}CHPh_2)(HN{=}CPh_2)(CO)_9]$ (**3**), *and* $[Os_3(\mu\text{-}H)\{\eta^2\text{-}HN{=}CPh(C_6H_4)\}(CO)_{10}]$ (**4**) *have been obtained by treatment of* $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ *and/or* $[Os_3(MeCN)_2(CO)_{10}]$ *with benzophenone imine. These compounds are unusual examples of metal clusters containing terminal imino (**1**, **3**), bridging amido (**2**, **3**), and orthometalated (chelating) imino (**4**) ligands derived from an N-unsubstituted organic imine.*

Introduction

In a previous work, we reported a high-yield synthesis of the triruthenium cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$,[1] a compound that contains a bridging imido (or 1-azavinylidene) ligand derived from benzophenone imine. Its efficient preparation and its stability under ambient conditions allowed us to study its reactivity toward phosphines,[1,2] alkynes,[3,4] protic acids,[2,5] hydrogen, silanes, and stannanes.[6] These studies afforded, among other noteworthy results, unprecedented examples of insertion reactions of nonactivated alkynes into metal−nitrogen bonds.[4]

Nowadays, metal cluster complexes containing imino or imido ligands derived from N-unsubstituted organic imines are still very rare. As far as we are aware, apart from $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ and its derivatives,[1−6] these complexes are restricted to a few examples of metals of the iron triad.[7−10] In the case of ruthenium, the only previously known compounds of this type are the triruthenium clusters $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CHR)(CO)_{10}]$, which were synthesized in low yields by treating nitriles with $[Ru_3(CO)_{12}]$ in the presence of carboxylic acids or molecular hydrogen.[8] For osmium, the number of reported compounds of this type is even more limited, being restricted to $[Os_3(HN{=}C_6H_{10})(CO)_{11}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}N{=}C_5H_8)(CO)_{10}]$, prepared by condensation of cyclohexanone with $[Os_3(NH_3)(CO)_{11}]$,[9a] and to products of reactions of activated nitriles with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[9b−d] Very recently, when the experimental part of our work was already finished, the synthesis of imino complexes of the type $[Os_3H(\mu\text{-}H)(HN{=}CHR)(CO)_{10}]$ (R = Me, Ph, $CHMe_2$, 2-furyl) by condensation of aldehydes with $[Os_3H(\mu\text{-}H)(NH_3)(CO)_{10}]$ has been published.[10]

The interesting derivative chemistry observed for $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$[1−6] and the absence in the literature of a related chemistry for osmium prompted us to attempt the synthesis of an analogous trinuclear osmium imido cluster. We describe here the reactivity of $[Os_3(CO)_{12}]$, $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, and $[Os_3(MeCN)_2(CO)_{10}]$ with benzophenone imine.

Results and Discussion

No reaction was observed between $[Os_3(CO)_{12}]$ and benzophenone imine even after long reaction times (3−5 h) at high temperature (refluxing toluene). In addition, treatment of this osmium cluster with the lithium salt of benzophenone imine, followed by titration with trifluoroacetic acid, led to an intractable mixture of compounds. Curiously, although $[Ru_3(CO)_{12}]$ does not react with benzophenone imine under thermal conditions either,[1] it gives $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ with good yield when it is sequentially treated with the lithium salt of benzophenone imine and trifluoroacetic acid.[1] These results led us to try the more reactive clusters $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Os_3(MeCN)_2(CO)_{10}]$ as the starting materials.

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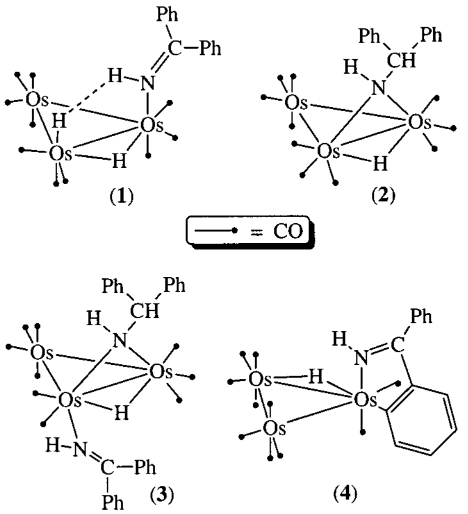
Chart 1



The unsaturated precursor $[\mathrm{Os_3}(\mu\text{-H})_2(\mathrm{CO})_{10}]$ reacted smoothly with benzophenone imine in THF at room temperature to give the trinuclear derivative $[\mathrm{Os_3H}(\mu\text{-H})(\mathrm{HN{=}CPh_2})(\mathrm{CO})_{10}]$ (**1**, Chart 1) in quantitative yield. Its ^{1}H NMR spectrum shows two singlet resonances in the high-field region, δ −9.91 and −15.84, indicating the presence of two inequivalent hydride ligands, while the hydrogen atom of the coordinated imine appears as a broad singlet at δ 9.93. These data, together with those obtained from microanalysis, FABMS investigations, and subsequent reactivity studies (vide infra), strongly support that complex **1** is isostructural with the complexes $[\mathrm{Os_3H}(\mu\text{-H})(\mathrm{HN{=}CHR})(\mathrm{CO})_{10}]$, formed by condensation of aldehydes with $[\mathrm{Os_3H}(\mu\text{-H})(\mathrm{NH_3})(\mathrm{CO})_{10}]$.[10] Using NMR methods, it has been proposed that the imino ligands of these complexes are coordinated in a terminal mode through the nitrogen atom, being stabilized by an interaction between the N−*H* hydrogen atom and the terminal hydride ligand of the molecule.[10] Unfortunately, despite many attempts, we could not get X-ray quality crystals of **1** to confirm this structure proposal. These data indicate that benzophenone imine behaves as a ligand in the same way as ammonia[11] and primary and secondary amines[12] in its reaction with $[\mathrm{Os_3}(\mu\text{-H})_2(\mathrm{CO})_{10}]$.

Thermolysis of **1** in refluxing 1,2-dichloroethane for 2 h led to a color change of the solution from yellow to brown. The ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of $[\mathrm{Os_3}(\mu\text{-H})_2(\mathrm{CO})_{10}]$ and three new products, subsequently identified as $[\mathrm{Os_3}(\mu\text{-H})(\mu\text{-HN{-}CHPh_2})(\mathrm{CO})_{10}]$ (**2**), $[\mathrm{Os_3}(\mu\text{-H})(\mu\text{-HN{-}CHPh_2})(\mathrm{HN{=}CPh_2})(\mathrm{CO})_9]$ (**3**), and $[\mathrm{Os_3}(\mu\text{-H})\{\eta^2\text{-HN{=}CPh(C_6H_4)}\}(\mathrm{CO})_{10}]$ (**4**) in ca. 2:2:1:1 ratio, respectively (Chart 1). When free benzophenone imine was added to the solution of **1** in 1,2-dichloroethane, the thermolysis led to compounds **2** and **3** in ca. 1:1 ratio, while $[\mathrm{Os_3}(\mu\text{-H})_2(\mathrm{CO})_{10}]$ and the orthometalated derivative **4** were not observed in the reaction mixture. All these products could be separated by chromatographic methods.

In a further attempt to prepare the osmium analogue of $[\mathrm{Ru_3}(\mu\text{-H})(\mu\text{-N{=}CPh_2})(\mathrm{CO})_{10}]$, the labile compound $[\mathrm{Os_3(MeCN)_2(CO)_{10}}]$ was treated with benzophenone imine. A 2 h reaction in refluxing THF rendered a mixture from which compound **4** was isolated in 35% yield. Similar results were obtained carrying out the reaction at room temperature after longer reaction times (12 h).

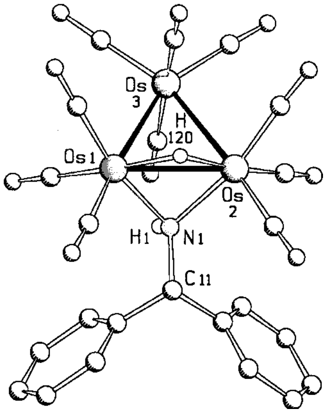


Figure 1. Molecular structure of compound **2**. Selected bond lengths (Å): Os(1)−Os(2) 2.798(1), Os(1)−Os(3) 2.846(1), Os(2)−Os(3) 2.840(1), Os(1)−N(1) 2.11(1), Os(2)−N(1) 2.10(1), N(1)−C(11) 1.50(1), mean Os−C$_{(\mathrm{CO})}$ 1.91(2), mean C−O 1.14(2).

The ^{1}H NMR spectrum of **2** shows the hydride resonance (δ −15.08) and the coupling (J = 12.4 Hz) of the N−*H* (δ 5.42) and C−*H* (δ 4.11) protons. The structure proposed for **2** in Chart 1 was confirmed by an X-ray diffraction study. Figure 1 shows a representation of this molecule. Relevant bond distances and angles are given in the figure caption. The compound, of approximately C_s symmetry, can be described as a triangle of osmium atoms with an edge doubly bridged by a hydride ligand and the nitrogen atom of the amido ligand. The molecule is completed with 10 carbonyl ligands. Full structural details are given in the Supporting Information. This structure was also suggested by the pattern of its IR spectrum in the carbonyl stretching region, which is similar to that of the ruthenium cluster $[\mathrm{Ru_3}(\mu\text{-H})(\mu\text{-HN{-}CHPh_2})(\mathrm{CO})_{10}]$, which was formed by hydrogenation of $[\mathrm{Ru_3}(\mu\text{-H})(\mu\text{-N{=}CPh_2})(\mathrm{CO})_{10}]$.[6] However, the structure of this ruthenium amido cluster has never been determined by diffraction methods.

The ^{1}H NMR spectrum of complex **3** shows a singlet resonance at δ −13.08, which can be assigned to a hydride ligand, while the hydrogen atom of the imino group appears as a broad singlet at δ 9.38. The benzene solvate compound was characterized by X-ray diffraction methods. The molecular structure is shown in Figure 2. Relevant bond distances and angles are given in the figure caption. The structure is similar to that of compound **2**, with an N-coordinated benzophenone imine replacing a carbonyl ligand in an equatorial position, cis to both the hydride and the amido ligands. Full structural details can be found in the Supporting Information. As far as we are aware, the only previous examples of clusters containing terminal N-unsubstituted imino ligands are the triosmium carbonyl clusters $[\mathrm{Os_3(HN{=}C_6H_{10})(CO)_{11}}]$[9a] and $[\mathrm{Os_3H}(\mu\text{-H})(\mathrm{HN{=}CHR})(\mathrm{CO})_{10}]$ (R = Me, Ph, CHMe$_2$, 2-furyl),[10] but they have not been characterized by diffraction methods. In these complexes, the terminal imino ligand appears to be stabilized by an intramolecular hydrogen-bonding interaction between the N−*H* fragment and the terminal

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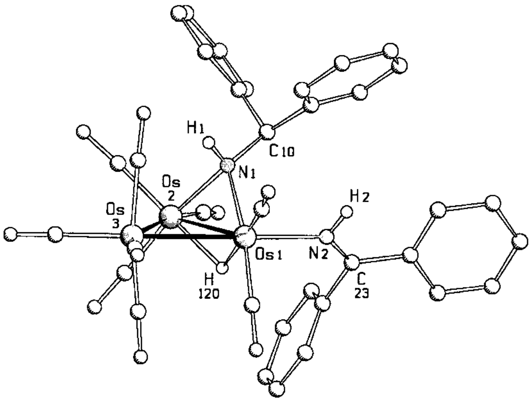

Figure 2. Molecular structure of compound **3**. Selected bond lengths (Å): Os(1)−Os(2) 2.815(1), Os(1)−Os(3) 2.842(1), Os(2)−Os(3) 2.852(1), Os(1)−N(1) 2.138(8), Os(2)−N(1) 2.124(7), Os(1)−N(2) 2.162(7), N(1)−C(10) 1.49(1), N(2)−C(23) 1.28(1), mean Os−$C_{(CO)}$ 1.89(4), mean C−O 1.16(2).

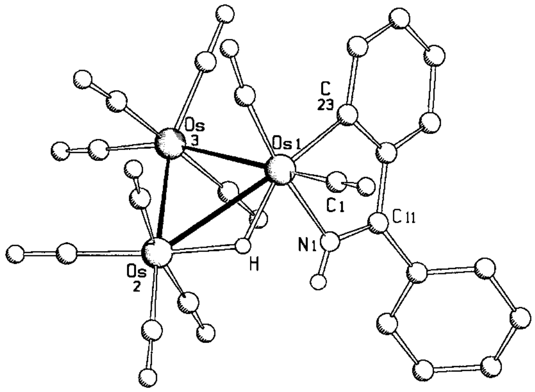

Figure 3. Molecular structure of compound **4**. Selected bond lengths (Å): Os(1)−Os(2) 3.034(3), Os(1)−Os(3) 2.893(3), Os(2)−Os(3) 2.902(2), Os(1)−N(1) 2.115(7), Os(1)−C(23) 2.076(9), N(1)−C(11) 1.30(1), mean Os−$C_{(CO)}$ 1.92(4), mean C−O 1.12(2).

hydride ligand. In the case of complex **3**, however, the X-ray diffraction data clearly show that this type of interaction is not present, at least in the solid state, since the hydrogen atom of the coordinated imine is positioned far away from the bridging hydride ligand.

The ^{1}H NMR spectrum of compound **4** shows a singlet resonance in the high-field region, at δ −16.58, which can be assigned to a hydride ligand, while a broad singlet at δ 9.13 is compatible with the presence of an N−*H* group. The spectrum also suggests the orthometalation of a phenyl ring, displaying signals in the range δ 8.16−7.01. Again, the spectroscopic data were not enough to unequivocally assign a structure, and an X-ray diffraction study was carried out. The structure of **4** is depicted in Figure 3. Relevant bond distances and angles are given in the figure caption. The structure consists of an Os_3 triangle attached to an orthometalated benzophenone imine ligand. The nitrogen atom of the imino ligand occupies an axial position, while the carbon atom of the orthometalated phenyl ring is attached to the same Os atom in an equatorial position. The hydride ligand spans the Os(1)−Os(2) bond, in a position approximately trans to the C(23)−Os(1) bond. The structure is completed with 10 carbonyl ligands. Full structural details can be found in the Supporting Information. Orthometalation of benzophenone imine has previously been observed in mononuclear complexes[13] and in one trinuclear Ru cluster.[1]

Conclusions

Four triosmium carbonyl cluster complexes containing imino and amido ligands derived from an N-unsubstituted organic imine have been prepared and characterized. Among them, compounds **1** and **3** are noteworthy because they contain a terminal imino ligand, a coordination mode that has been very rarely observed for N-unsubstituted organic imines.[9a,10] Compounds **2** and **3** contain bridging amido ligands which result from a thermally induced intramolecular hydrogen transfer process within **1**. Orthometalation (C−H bond activation) is preferred over N−H bond activation when benzophenone imine is treated with $[Os_3(MeCN)_2(CO)_{10}]$, leading to compound **4**. Unfortunately, the osmium analogue of $[Ru_3(\mu\text{-H})(\mu\text{-N=CPh}_2)(CO_{10}]$ still remains unknown.

Experimental Section

General Comments. Solvents were dried over sodium benzophenone ketyl (THF, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. Unless otherwise stated, the reactions were performed under nitrogen at room temperature. $[Os_3(\mu\text{-H})_2(CO)_{10}]$ was prepared as described previously.[14] All other reagents were obtained from commercial sources. NMR spectra were recorded at room temperature with Bruker AC-200 or AC-300 instruments, using $SiMe_4$ as internal standard (δ 0). FABMS were obtained from the University of Santiago de Compostela Mass Spectroscopic Service; data given refer to the most abundant molecular ion isotopomer. Microanalyses were obtained from the University of Oviedo Analytical Service.

Synthesis of $[Os_3H(\mu\text{-H})(NH{=}CPh_2)(CO)_{10}]$ (1). An excess of benzophenone imine (0.1 mL) was added to a solution of $[Os_3(\mu\text{-H})_2(CO)_{10}]$ (200 mg, 0.235 mmol) in 20 mL of dichloromethane. The color changed instantaneously from violet to pale yellow. After stirring for 10 min, the solvent was removed under reduced pressure. The residue was washed with hexanes (1 × 5 mL) to afford compound **1** as a yellow solid (242 mg, 100%). Calcd for $C_{23}H_{13}NO_{10}Os_3$ (1033.96): C, 26.77; H, 1.27; N, 1.36. Found: C, 26.70; H, 1.30; N, 1.33. FABMS (*m/z*): 1035 [M^+]. IR (CH_2Cl_2): ν(CO) 2100 (m), 2061 (vs), 2048 (vs), 2020 (s), 2001 (s), 1984 (m, sh), 1964 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 9.93 (s, br, 1 H, N*H*), 7.67−7.28 (m, 10 H, Ph_2), −9.91 (s, 1 H, Os−*H*), −15.84 (s, 1 H, μ-H) ppm.

Thermolysis of Compound 1. Complex **1** (100 mg, 0.097 mmol) was dissolved in 20 mL of 1,2-dichloroethane, and the mixture was stirred at reflux temperature for 2 h. The color changed from yellow to brown. The solvent was removed under reduced pressure to give a brown residue. ^{1}H NMR monitoring of this residue showed the presence of compounds $[Os_3(\mu\text{-H})_2(CO)_{10}]$, **2**, **3**, and **4** in ca. 2:2:1:1 ratio. The residue was dissolved in 2 mL of dichloromethane and was transferred to a silica gel chromatography column (30 × 2 cm). Two bands

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Table 1. Crystal Data and Details of Measurements for Compounds 2, 3·C_6H_6, and 4

	2	**3**·C_6H_6	4
formula	$C_{23}H_{13}NO_{10}Os_3$	$C_{41}H_{30}N_2O_9Os_3$	$C_{23}H_{11}NO_{10}Os_3$
fw	1033.94	1265.27	1031.93
cryst syst	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/n$
a, Å	23.472(5)	11.029(1)	13.00(1)
b, Å	11.120(3)	12.278(1)	12.548(7)
c, Å	20.593(6)	15.922(2)	16.36(1)
α, deg	90	101.681(4)	90
β, deg	106.98(2)	106.035(3)	108.97(8)
γ, deg	90	94.080(4)	90
V, Å^3	5151(2)	2010(4)	2524(3)
Z	8	2	4
$F(000)$	3728	1180	1856
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
D_{calcd}, g cm^{-3}	2.672	2.090	2.716
μ(Mo Kα), mm^{-1}	14.85	9.51	15.12
min−max transmn	0.48−1.00[a]	0.23−1.00[b]	0.69−1.00[a]
cryst size, mm^3	0.22 × 0.18 × 0.18	0.20 × 0.16 × 0.16	0.18 × 0.18 × 0.16
temp, K	293(2)	293(2)	293(2)
θ limits, deg	3.0−25.0	1.37−30.00	3.0−25.0
min/max h, k, l	−27/26, 0/13, 0/24	−15/15, −17/15,−21/22	−15/14, 0/14, 0/19
no. of rflns measd	9763	24 718	4594
no. of unique rflns	4465	11 680	4432
no. of rflns $I > 2\sigma(I)$	3680	5443	3542
no. of params	314	437	334
GOF on F^2	0.985	0.803	1.018
R_1 (on F, $I > 2\sigma(I)$)	0.0526	0.0502	0.0349
wR_2 (on F^2, all data)	0.1482	0.1141	0.0931

[a] ψ-scan absorption correction. [b] Bruker area detector absorption correction.

were eluted using a mixture of hexanes/toluene (5:1) as eluant. The first band, violet, was subsequently identified as $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (^{1}H NMR, IR). The second band, yellow, afforded compound **2** (15 mg, 15%). Further elution with a mixture of hexanes/dichloromethane (4:1) gave two additional bands. The third fraction, orange, afforded complex **3** (10 mg, 9%). The fourth band, pale yellow, contained complex **4** (10 mg, 10%).

Spectroscopic data for 2: Calcd for $C_{23}H_{13}NO_{10}Os_3$ (1033.94): C, 26.72; H, 1.27; N, 1.35. Found: C, 26.85; H, 1.11; N, 1.28. FABMS (m/z): 1035 [M$^+$]. IR (CH_2Cl_2): ν(CO) 2103 (w), 2067 (vs), 2050 (s), 2017 (s), 1999 (m), 1988 (m), 1975 (w, sh) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.40−7.17 (m, 10 H, Ph_2), 5.42 (d, br, J = 12.4 Hz, 1 H N*H)*, 4.11 (d, J = 12.4 Hz, 1 H C*H)*, −15.08 (s, 1 H, μ-H) ppm.

Spectroscopic data for 3: Anal. Calcd for $C_{35}H_{24}N_2O_9Os_3$ (1187.19): C, 35.46; H, 2.04; N, 2.36. Found: C, 35.71; H, 1.90; N, 2.30. FABMS (m/z): 1188 [M$^+$]. IR (CH_2Cl_2): ν(CO) 2121 (w), 2085 (m), 2046 (vs), 2005 (s), 1992 (s), 1966 (m), 1923 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 9.38 (s, br, 1 H, N*H*), 7.59−7.00 (m, 20 H, Ph_4), 5.35 (d, br, J = 12.8 Hz, 1 H N*H)*, 4.15 (d, J = 12.8 Hz, 1 H C*H)*, −13.08 (s, 1 H, μ-H) ppm.

Spectroscopic data for 4: Anal. Calcd for $C_{23}H_{11}NO_{10}Os_3$ (1031.93): C, 26.77; H, 1.07; N, 1.36. Found: C, 26.86; H, 1.10; N, 1.37. FABMS (m/z): 1033 [M$^+$]. IR (CH_2Cl_2): ν(CO) 2124 (w), 2064 (m), 2050 (m), 2035 (vs), 2023 (m, sh), 1992 (s), 1984 (m, sh), 1917 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.13 (s, br, 1 H, N*H*), 8.16 (d, J = 7.6 Hz, 1 H), 7.65−7.51 (m, 6 H), 7.25 (t, J = 7.6 Hz, 1 H), 7.01 (t, J = 7.6 Hz, 1 H), −16.58 (s, 1 H, μ-H) ppm.

Reaction of $[Os_3(MeCN)_2(CO)_{10}]$ with HN=CPh$_2$. Anhydrous Me_3NO (19 mg, 0.254 mmol) was added to a suspension of $[Os_3(CO)_{12}]$ (100 mg, 0.110 mmol) in 60 mL of acetonitrile over a period of 2 h. The resulting solution was stirred for a further 1 h, and the solvent was removed under reduced pressure. The residue was dissolved in 30 mL of THF. Benzophenone imine (28 μL, 0.165 mmol) was added, and the solution was heated at reflux temperature for 2 h. The solvent was then removed under reduced pressure to give an orange residue. The ^{1}H NMR spectrum of this residue showed the presence of compound **4**, together with some minor unidentified impurities. The solid residue was dissolved in 2 mL of dichloromethane, and the solution was transferred to a silica gel chromatography column (20 × 1.5 cm). A mixture of hexanes/dichloromethane (5:1) was used as eluant. The compound isolated from the first band, orange, remains unidentified. The second band, orange, contained compound **4** (40 mg, 35%).

Crystal Structure Determination of Compounds 2, 3·C_6H_6, and 4. Crystal data and details of measurements are summarized in Table 1.

X-ray diffraction data collections were carried out on a NONIUS CAD-4 diffractometer (compounds **2** and **4**) and on a Bruker area detector diffractometer (compound **3**·C_6H_6). Structures were solved by direct methods followed by difference Fourier syntheses and full-matrix least-squares refinement on F^2 using SHELXL97.[15a] All non-H atoms were treated anisotropically. Absorption correction for **2** and **4** was applied by azimuthal scanning of high χ reflections. H atoms bound to N and C atoms were added in calculated positions and refined riding on their respective N and C atoms. The positions of the hydride atoms were estimated using the program XHYDEX;[15b] their coordinates were included in the Fourier calculations but not refined. The approximate location of the H(hydride) atoms was also detectable by visual inspection of space-filling plots of the three molecules: suitable niches were invariably found corresponding to the calculated positions. The program SCHAKAL97[15c] was used for all graphical representations.

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Supporting Information Available: ORTEP drawings, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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