Reactivity of the Anionic Carbonyltrirhenium Cluster $[Re_3(\mu\text{-}H)_3\text{-}(\mu_3\text{-}ampy)(CO)_9]^-$ − Synthesis of Neutral Phosphane and Alkenyl Derivatives

Javier A. Cabeza,*[a] Fabrizia Grepioni,*[b] Angela Llamazares,[a] Víctor Riera,[a] and Rajiv Trivedi[a]

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Protonation of the trinuclear anionic rhenium cluster $[HNEt_3][Re_3(\mu\text{-}H)_3(\mu_3\text{-}ampy)(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) with $[HOEt_2][BF_4]$ at low temperature leads to dihydrogen and the neutral unsaturated dihydride derivative $[Re_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_9]$. The low thermal stability of this compound (it undergoes decomposition above 5 °C) has prevented its isolation as a pure solid. The compound $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ is the major product obtained when the protonation of **1** is carried out under CO. Protonation of **1** in the presence of phosphanes or alkynes gives the neutral derivatives $[Re_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(PR_3)(CO)_9]$ (**2**: R = Ph; **3**: R = *p*-tolyl) or $[Re_3(\mu_3\text{-}H)(\mu_3\text{-}ampy)(\mu\text{-}RC{=}CHR')(CO)_9]$ (**4**: R = R′ = Ph; **5**: R = R′ =Et; **6a**: R = Ph, R′ = H; **6b**: R = H, R′ = Ph). In **2** and **3**, the phosphane ligand is in an equatorial position on an Re atom of the NH-bridged Re–Re edge, *cis* to a hydride ligand and far away from the other hydride ion. In compounds **4**–**6**, the alkenyl ligand, which arises from the insertion of the corresponding alkyne into an Re–H bond, is attached to two metal atoms in a $\mu\text{-}\eta^1{:}\eta^2$ fashion, spanning the same Re–Re edge as the NH fragment of the ampy ligand. The hydride ligand of compounds **4**–**6** coordinates in a triply bridging fashion, capping the Re_3 triangle. Compounds **4**–**6** represent the first examples of trirhenium clusters containing alkenyl ligands.

Introduction

Until now, few carbonyl cluster compounds (three or more metal atoms connected by metal−metal bonds) of rhenium are known,[1] in comparison to those known for ruthenium and osmium.[2] This is undoubtedly due to the lack of a convenient rhenium cluster precursor. In fact, with few exceptions,[3] the cluster compounds made from $[Re_2(CO)_{10}]$, the most readily available carbonylrhenium complex, can only be isolated in medium to low yield.[4−6] For example, $[Re_3(\mu\text{-}H)_3(CO)_{12}]$, which is isoelectronic with the most important ruthenium and osmium starting clusters $[M_3(CO)_{12}]$ (M = Ru, Os), is prepared from $[Re_2(CO)_{10}]$ either by hydrogenation[4a] or treatment with $Na[BH_4]$ followed by acidification,[5d,5e] but both procedures are rather tedious and the yields are only moderate. Moreover, $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ is kinetically very stable and most of its reactions require high temperatures (which promote changes in cluster and/or ligand integrity, often leading to mixtures of products)[1] or derivatization to the more reactive $[Re_3(\mu\text{-}H)_3(CO)_{10}(MeCN)_2]$.[7] Ciani, D'Alfonso and co-workers have extensively studied the derivative chemistry of the anionic unsaturated cluster $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$,[1] but its best preparation requires a high pressure hydrogenation (100 atm) of $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$,[8] which is made by deprotonation of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$.[9] In addition, the unsaturated cluster $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$, which can be made by hydrogenation of $[Re_2(CO)_{10}]$,[4a] is so reactive that its reactions are generally not very selective, often leading to mixtures of many products.[10]

We have recently reported that the anionic carbonyltrirhenium cluster $[HNEt_3][Re_3(\mu\text{-}H)_3(\mu_3\text{-}ampy)(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) can be prepared in fair yield (70%) from $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]$, Hampy and triethylamine.[10] It should be noted that in carbonylruthenium cluster compounds, as for example $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_9]$,[11] face-bridging 2-aminopyridinato ligands help maintain the cluster integrity and provide reaction pathways of low activation energy.[12] In fact, over a hundred carbonylruthenium clusters containing μ_3-2-aminopyridinato ligands have already been prepared,[2a] including some efficient catalyst precursors for alkyne hydrogenation,[13] dimerization[14] and polymerization[14] reactions.

All the above-mentioned data prompted us to study the reactivity of compound **1**. We have already investigated the synthesis of tetranuclear Re_3Au clusters by reactions of **1** with gold complexes.[15] We now report its protonation reaction as well as the preparation of some neutral phosphane and alkenyl derivatives. The latter represent the first examples of trirhenium clusters containing alkenyl ligands.

Results and Discussion

Protonation Reaction of Compound 1

Compound **1** was found to be very stable toward nucleophilic reagents. No reaction was observed when **1** was

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[a] Departamento de Química Orgánica e Inorgánica,
Instituto de Química Organometálica “Enrique Moles”,
Universidad de Oviedo, 33071 Oviedo, Spain
E-mail: jac@sauron.quimica.uniovi.es
Fax: (internat.) + 34-985/103446
[b] Dipartimento di Chimica, Universitá di Sassari,
via Vienna 2, 07100 Sassari, Italy
E-mail: grepioni@ssmain.uniss.it

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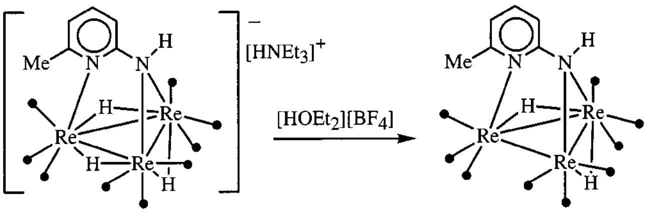
treated with phosphane, nitrile or alkyne reagents in THF at reflux temperature. Its anionic character and the fact that it is a saturated 48-electron trinuclear cluster may account (at least in part) for its stability toward nucleophilic reagents.

Interestingly, an instantaneous reaction was observed when compound **1** was treated with $[HOEt_2][BF_4]$: The color changed from colorless to yellow, a gas was evolved and drastic changes were observed in the IR spectrum of the solution. Unfortunately, no pure products could be isolated from this reaction, regardless of the solvent (THF, dichloromethane, acetonitrile) and the ratio of the reactants.

In order to obtain some insight of this reaction, the protonation was subsequently monitored by ^1H NMR spectroscopy at low temperature. A single product was observed upon mixing the reagents in CD_2Cl_2 at −78 °C, characterized by two uncoupled hydride resonances of equal intensity at $\delta = -7.85$ and -8.53, in addition to a set of resonances due to the ampy ligand. This compound remained unchanged upon warming the solution to 5 °C but, unfortunately, it decomposed to other products above this temperature.

These data suggest that the protonation of compound **1** results in the release of dihydrogen and in the formation of the neutral species $[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9]$. The asymmetric structure proposed for this species in Scheme 1 is in agreement with the observation of two hydride resonances in the ^1H NMR spectrum. Its coordinative unsaturation (46-electron) may be responsible for its low thermal stability. Although the use of coordinating solvents (THF, acetonitrile) did not lead to the isolation of solvated derivatives as pure products, some phosphane and alkyne derivatives could be isolated carrying out the protonation in the presence of the appropriate ligands (vide infra). The structures of these derivatives are also in agreement with that proposed for $[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9]$ in Scheme 1.

Treatment of a solution of compound **1** in dichloromethane with $[HOEt_2][BF_4]$ under carbon monoxide led to a transient color change of the initial colorless solution to pale yellow, but it returned to colorless within a few seconds. An appropriate workup of this solution allowed the isolation of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ as the major carbonyl complex of the reaction mixture. This result, which may seem of little relevance, is indeed quite interesting, since it reveals that in carbonylrhenium cluster chemistry the triply bridging ampy ligand can be removed under mild conditions and, therefore, it should not be expected to maintain the trinuclear cluster integrity as efficiently as it does in ruthenium cluster chemistry.[11−14]



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Scheme 1. Protonation of compound **1**

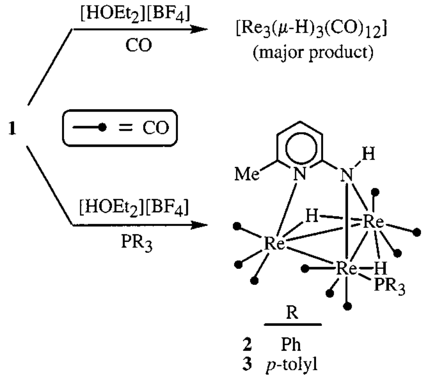
Neutral Phosphane Derivatives of Compound 1

Protonation of a dichloromethane solution of complex **1** with $[HOEt_2][BF_4]$ in the presence of triphenylphosphane (1:1:1 mol ratio) led to the immediate formation of the yellow neutral derivative $[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(PPh_3)(CO)_9]$ (**2**). Its formulation was clearly evidenced by its microanalysis and spectroscopic data. Its ^1H NMR spectra shows two hydride resonances, one as a doublet of doublets ($\delta = -9.50$, $J = 12.3$ and 1.6 Hz) and the other as a small doublet ($\delta = -9.92$, $J = 1.6$ Hz), indicating that the compound has two hydride ligands which couple slightly to each other (1.6 Hz) and that only one of them couples to the phosphorus atom ($J = 12.3$ Hz). As this J_{P-H} coupling value is typical of a *cis* arrangement of hydride and phosphane ligands in trinuclear metal clusters,[16] and as no coupling is observed between the other hydride ion and the phosphorus atom, we propose the structure depicted in Scheme 2 for this complex. No crystals of compound **2** suitable for an X-ray diffraction study could be obtained.

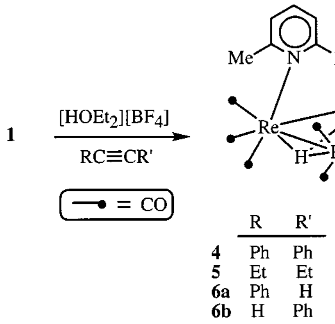
As the structure proposed for compound **2**, although reasonable, is not unambiguous, we decided to prepare an analogous derivative, containing a different phosphane ligand, in an attempt to obtain X-ray diffraction-quality crystals. The compound $[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})\{P(p\text{-tolyl})_3\}(CO)_9]$ (**3**) was made by a similar procedure as that used for **2**. Its analytical and spectroscopic data indicate that it is isostructural with complex **2**, but, unfortunately, it could not be crystallized.

It seems clear that compounds **2** and **3** are formed upon coordination of the corresponding phosphane to the unsaturated species that results when complex **1** is protonated and dihydrogen is released.

The number of previously described phosphane derivatives of trirhenium clusters is very small, and most of them are simple phosphane-substituted derivatives of carbonyl hydrido clusters.[1,17] The anionic formimidoyl complex $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH{=}NC_6H_{11})(PMe_2Ph)(CO)_9]^-$ is the only previous example of a trirhenium cluster containing both N-donor and P-donor ligands.[18]



Scheme 2. Protonation of compound **1** in the presence of CO and phosphane ligands



Scheme 3. Synthesis of neutral alkenyl derivatives

Neutral Alkenyl Derivatives of Compound 1

Protonation of compound **1** with $[HOEt_2][BF_4]$ in the presence of diphenylacetylene, 3-hexyne or phenylacetylene led to the neutral alkenyl derivatives $[Re_3(\mu_3\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}RC{=}CHR')(CO)_9]$ (**4**: R = R′ = Ph; **5**: R = R′ = Et; **6a**: R = Ph, R′ = H; **6b**: R = H, R = Ph) (Scheme 3). Compounds **4** and **5** were obtained as pure products, but the isomeric compounds **6a** and **6b** were obtained as an inseparable mixture. These results suggest that the reaction is quite general since it works well for internal, terminal, aryl- and alkylalkynes, giving a mixture of two isomers when the alkyne used is not symmetric. In these compounds, the alkenyl ligands arise from the coordination of the corresponding alkyne to the unsaturated species formed by protonation of compound **1**, followed by a migratory insertion of the alkyne into a Re−H bond.

The compounds were characterized by analytical and spectroscopic methods. All have similar IR and NMR spectra, indicating that they have a common structure. The most relevant features of their ^1H NMR spectra are (a) the presence of a resonance due to the vinyl hydrogen atom in the range δ = 6−3, as observed for many complexes of other metals containing bridging alkenyl ligands,[13,14] and (b) the observation of only one hydride resonance as a small doublet (J = 3.0 Hz in all cases except for **6b**, which was observed as a singlet). Decoupling experiments revealed that such a doublet arises from the coupling of the hydride with the hydrogen atom of the NH fragment of the ampy ligand (which is observed as a broad singlet in the ^1H NMR spectrum at room temperature). The fact that the hydride ligand signal of **6b** is observed as a singlet suggests that its structure may differ from that of the other alkenyl derivatives, but we have been unable to investigate this matter further because compounds **6a** and **6b** were always obtained as a mixture.

The analytical and spectroscopic data of these alkenyl derivatives were not sufficient to unequivocally assign the positions of the hydride and alkenyl ligands in the clusters. Therefore, an X-ray diffraction study was required. None of the compounds crystallized well, nonetheless, in the case of compound **4**, we managed to obtain crystals of sufficient quality for the diffraction experiment. The molecular structure of compound **4** is shown in Figure 1, together with the labeling scheme and selected bond length parameters. The ampy ligand coordinates to the Re_3 triangle in a capping mode, previously observed in many trinuclear clusters.[10−16] The alkenyl ligand spans the same Re−Re edge as the amido fragment of the ampy ligand. The carbonyl ligands are bound to the cluster in a terminal fashion, three to each Re atom. Although the hydride location could not be directly obtained from the diffraction data, calculations with the program XHYDEX[19] revealed a minimum energy position for the hydride ligand in a triply bridging site, capping the metal triangle as shown in Figure 1 and Scheme 3. Triply bridging hydrides are frequently observed in carbonylrhenium clusters.[1]

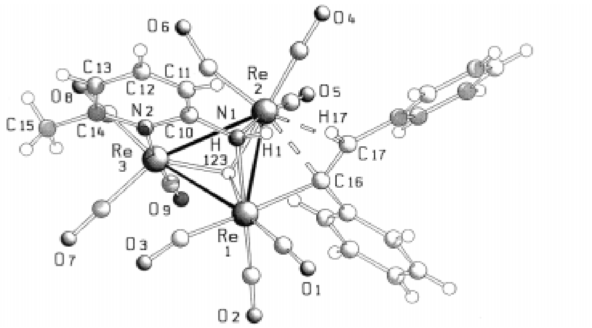


Figure 1. Molecular structure of $[Re_3(\mu_3\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}PhC{=}CHPh)(CO)_9]$ (**4**); selected bond lengths [Å]: Re(1)−Re(2) 2.853(2), Re(1)−Re(3) 3.018(2), Re(2)−Re(3) 3.054(2), Re−H(123) 1.88, 1.88, 1.90, Re(1)−C(16) 2.20(2), Re(2)−C(16) 2.30(2), Re(2)−C(17) 2.45(2), Re(1)−N(1) 2.16(2), Re(2)−N(1) 2.17(2), Re(3)−N(2) 2.27(2), mean $Re-C_{(CO)}$ 1.914, mean C−O 1.165

The reactions leading to compounds **4−6** can be regarded as pioneering processes in the so far unreported field of the reactivity of carbonyltrirhenium clusters with unsaturated hydrocarbons. In fact, compounds **4−6** are the first examples of trirhenium clusters containing alkenyl ligands.

Experimental Section

General: Solvents were dried with sodium diphenyl ketyl (hydrocarbons) or calcium hydride (dichloromethane) and distilled under nitrogen prior to 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 by spot TLC (silica gel). − Compound **1** was prepared by a published procedure,[10] all other reagents were purchased as analytically pure samples. − IR spectra were recorded with a Perkin−Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. − ^1H and $^{31}P\{^1H\}$ NMR spectra were run at room temperature with Bruker AC-200 and AC-300 instruments, being referenced to internal $SiMe_4$ (for ^1H: δ = 0) or external aqueous 85% H_3PO_4 (for ^{31}P: δ = 0). − Microanalyses were obtained from the University of Oviedo Analytical Service.

Protonation of Compound 1: A 5-mm NMR tube was charged under nitrogen with compound **1** (0.012 g) and CD_2Cl_2 (0.5 mL) and immersed in a bath kept at −78 °C. Addition of $[HOEt_2][BF_4]$ (2 μL) to the cold solution led to a color change from colorless to yellow. The tube was quickly transferred to the NMR probe, previously cooled at −80 °C. The resonances of a pure product were observed at δ = −8.53 (s, 1 H, μ-H), −7.85 (s, 1 H, μ-H), 2.78 (s, 3 H, ampy-Me), 6.44 (s, br, 1 H, ampy-N*H*), 6.76 (d, 7.6 Hz, 1 H, ampy-C*H*), 6.87 (d, 7.6 Hz, 1 H, ampy-C*H*), 7.50 (t, 7.6 Hz, 1 H, ampy-C*H*) ppm. This product could not be isolated.

Protonation of Compound 1 under Carbon Monoxide: A solution of compound **1** (0.025 g, 0.024 mmol) in dichloromethane (10 mL) was treated with $[HOEt_2][BF_4]$ (3.5 μL, 0.025 mmol) while the solution was kept under carbon monoxide. The initially colorless solution changed to pale yellow upon addition of the acid, but it soon returned to colorless. After being stirred for 3 h, the IR spectrum of the solution showed the presence of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$. The solvent was removed under reduced pressure and the residue was extracted into hexane (3 × 5 mL). The extract was concentrated to dryness to give a colorless solid which was found to be $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (IR, ^1H NMR). The fraction insoluble in hexane contained $[HNEt_3][BF_4]$ and Hampy among other minor products (IR, ^1H NMR).

$[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(PPh_3)(CO)_9]$ (2): $[HOEt_2][BF_4]$ (3 μL, 0.021 mmol) was added to a dichloromethane solution (10 mL) of compound **1** (0.023 g, 0.022 mmol) and PPh_3 (0.006 g, 0.023 mmol). The color changed from colorless to yellow. The solution was stirred for 2 h and concentrated to dryness. The solid residue was extracted with toluene (3 × 5 mL). The extract was concentrated to dryness and the residue was crystallized from dichloromethane/hexane to give compound **2** as a yellow solid (0.015 g, 58%). − $C_{33}H_{24}N_2O_9PRe_3$ (1182.16): calcd. C 33.53, H 2.05, N 3.37; found C 33.64, H 2.13, N 3.16. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2049 (m), 2017 (vs), 1949 (m), 1938 (m), 1923 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): $\delta = -9.92$ (d, J = 1.6 Hz, 1 H, μ-H), −9.50 (dd, 12.3 and 1.6 Hz, 1 H, μ-H) 2.59 (s, 3 H, ampy-Me), 4.88 (s, br, 1 H, ampy-N*H*), 5.59 (d, J = 7.7 Hz, 1 H, ampy-C*H*), 6.51 (d, J = 7.7 Hz, 1 H, ampy-C*H*), 6.87 (t, J = 7.7 Hz, 1 H, ampy-C*H*), 7.5−7.1 (m, 15 H, 3 Ph). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 1.4 (s).

$[Re_3(\mu\text{-}H)_2(\mu_3\text{-ampy})\{P(p\text{-tolyl})_3\}(CO)_9]$ (3): This compound was prepared as described above for compound **2**. Reagents: **1** (0.021 g, 0.020 mmol), $P(p\text{-tolyl})_3$ (0.007 g, 0.022 mmol), $[HOEt_2][BF_4]$ (3 μL, 0.021 mmol). Yellow solid (0.014 g, 57%). − $C_{36}H_{30}N_2O_9PRe_3$ (1224.24): calcd. C 35.32, H 2.47, N 2.29; found C 35.54, H 2.66, N 2.12. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2049 (m), 2017 (vs), 1949 (m), 1940 (m), 1919 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): $\delta = -9.93$ (d, J = 1.3 Hz, 1 H, μ-H), −9.50 (dd, J = 11.0 and 1.3 Hz, 1 H, μ-H), 2.40 (s, 9 H, 3 Me), 2.57 (s, 3 H, ampy-Me), 4.87 (s, br, 1 H, ampy-N*H*), 5.63 (d, J = 7.7 Hz, 1 H, ampy-C*H*), 6.51 (d, J = 7.7 Hz, 1 H, ampy-C*H*), 6.86 (t, J = 7.7 Hz, 1 H, ampy-C*H*), 7.6−7.2 (m, 12 H, 3 C_6H_4). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -0.77$ (s).

$[Re_3(\mu_3\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}PhC{=}CHPh)(CO)_9]$ (4): $[HOEt_2][BF_4]$ (5 μL, 0.035 mmol) was added to a dichloromethane solution (10 mL) of compound **1** (0.035 g, 0.034 mmol) and diphenylacetylene (0.007 g, 0.039 mmol). The color changed from colorless to orange. The solution was stirred for 1 h and was concentrated to dryness. The solid residue was extracted with toluene (2 × 5 mL). The extract was concentrated to dryness and the residue was crystallized from dichloromethane/hexane to give compound **4** as an orange solid (0.024 g, 64%). − $C_{29}H_{19}N_2O_9Re_3$ (1098.10): calcd. C 31.72, H 1.74, N 2.55; found C 32.00, H 1.82, N 2.43. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2055 (w), 2027 (vs), 2016 (s), 1956 (m), 1946 (sh), 1924 (sh) cm^{-1}. − ^1H NMR ($CDCl_3$): $\delta = -6.10$ (d, J = 3.0 Hz, 1 H, μ_3-H), 2.88 (br, 1 H, ampy-N*H*), 3.06 (s, 3 H, ampy-Me), 4.86 (s, 1 H, alkenyl-C*H*), 7.6−6.5 (m, 12 H, 2 Ph + 2 ampy-C*H*).

$[Re_3(\mu_3\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}EtC{=}CHEt)(CO)_9]$ (5): This compound was prepared as described above for compound **4**. Reagents: **1** (0.060 g, 0.059 mmol), 3-hexyne (8 μL, 0.070 mmol), $[HOEt_2][BF_4]$ (9 μL, 0.063 mmol). Orange solid (0.038 g, 64%). − $C_{21}H_{19}N_2O_9Re_3$ (1002.01): calcd. C 25.17, H 1.91, N 2.80; found C 25.20, H 2.01, N 2.72. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2055 (w), 2028 (vs), 2009 (s), 1958 (m), 1937 (sh), 1926 (m) cm^{-1}. − ^1H NMR ($CDCl_3$): $\delta = -8.97$ (d, J = 3.0 Hz, 1 H, μ_3-H), 1.25 (m, 6 H of 2 Et), 2.30 (m, 2 H of Et), 2.77 (q, J = 6.2 Hz, 2 H of Et), 3.07 (s, 3 H, ampy-Me), 4.31 (br, 1 H, ampy-N*H*), 5.68 (t, J = 6.1 Hz, 1 H, alkenyl-C*H*), 6.80 (d, J = 7.6 Hz, 1 H, ampy-C*H*), 6.87 (d, J = 7.6 Hz, 1 H, ampy-C*H*), 7.46 (t, J = 7.6 Hz, 1 H, ampy-C*H*).

$[Re_3(\mu_3\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}PhC{=}CH_2)(CO)_9]$ (6a) and $[Re_3(\mu_3\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}HC{=}CHPh)(CO)_9]$ (6b): These compounds were prepared as a 1:1 mixture, as described above for compound **4**. Reagents: **1** (0.025 g, 0.024 mmol), phenylacetylene (3 μL, 0.026 mmol), $[HOEt_2][BF_4]$ (4 μL, 0.028 mmol). Orange solid (0.012 g, 49%). − $C_{23}H_{15}N_2O_9Re_3$ (1022.01): calcd. C 27.03, H 1.48, N 2.74; found C 27.32, H 1.66, N 2.55. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2056 (w), 2026 (vs), 2017 (s), 1957 (m), 1941 (sh), 1936 (sh) cm^{-1}. − Selected ^1H NMR ($CDCl_3$) data for **6a** (extracted from the spectrum of the mixture): $\delta = -6.36$ (d, J = 3.0 Hz, 1 H, μ_3-H), 2.06 (s, 1 H, alkenyl-C*H*), 3.06 (s, 1 H, alkenyl-C*H*). − Selected ^1H NMR ($CDCl_3$) data for **6b** (extracted from the spectrum of the mixture): $\delta = -7.69$ (s, 1 H, μ_3-H), 4.74 (d, J = 5.0 Hz, 1 H, alkenyl-C*H*), 7.19 (d, J = 5.0 Hz, 1 H, alkenyl-C*H*).

Crystal Structure of Compound 4: X-ray diffraction data was collected at room temperature with a Nonius CAD-4 diffractometer equipped with a graphite monochromator [$\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å]. Crystal data and details of measurement: $C_{29}H_{19}N_2O_9Re_3$, M = 1098.06, monoclinic $P2_1/n$, a = 11.450(4), b = 24.150(8), c = 12.344(4) Å, β = 116.89(3)°, V = 3044(1) $Å^3$, Z = 4, $F(000)$ = 2016, D_c = 2.396 g cm^{-3}, μ = 11.954 mm^{-1}, measured refl.s 4218, unique refl.s = 4199, 209 parameters, R_1[on F, 2401 $I > 2\sigma(I)$] = 0.0641, R_w(on F^2, all data) = 0.1757, GoF = 0.998. The structure was solved by direct methods followed by difference Fourier syntheses and full-matrix least-squares refinement on F^2, using SHELXL97.[20a] Due to decay of the poorly diffracting crystal, the resulting data set contained a limited number of reflections with sufficient intensity; rigid constraints were applied to the phenyl groups and only rhenium and oxygen atoms were treated anisotropically. Absorption correction was applied by azimuthal scanning of high χ reflections (min.−max. absorption correction 0.67−1.00). H atoms bound to C atoms were added in calculated positions and were refined riding on their respective C atoms. The H atom bound to the N atom was directly located from a Fourier map and was not refined. The position of the hydride H atom was calculated using the program XHYDEX[19] and its coordinates were included in the Fourier calculations but not refined. Visual inspection of space filling diagrams of the molecule also allowed approximate location of the hydride H atom position, since a suitable niche was found in accordance with the calculated position. The program SCHAKAL97[20b] was used for the molecular graphical representation. Crystallographic data (excluding structure factors) for compound **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140540. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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