brown material that proved to be insoluble in all common organic solvents.

For **17**: ^{31}P NMR δ 33.2 (s, half-height peak width 92 Hz), -8.1 (s, half-height peak width 126 Hz) ppm.

X-ray Structure Determination Technique. Our general technique is described elsewhere[14] and only details related to the present work will be given here. Crystals of **1** were grown by the slow diffusion of hexanes into a toluene–hexanes solution of **1** at -20 °C. Crystals of **4** and **6** were obtained by cooling toluene–hexanes solutions to -20 °C. A summary of the important crystallographic data is presented in Table I.

The structures were solved by a combination of direct methods (using MULTAN 82[32]) and Fourier methods. All structures were refined by full-matrix, least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms except for **7** in which the O, N, and C atoms were refined isotropically. In the case of **1**, difference Fourier syntheses, calculated toward the end of refinement, showed maxima consistent with the expected positions of H atoms. These H atoms were included in the refinement.

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Supplementary Material Available: Figures showing crystal structures for **1**, **5**, and **7** with complete labeling of non-hydrogen atoms and tables giving complete positional and thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters for **1**, **5**, and **7** and hydrogen atom coordinates for **1** (41 pages); tables of calculated and observed structure factors for **1**, **5**, and **7** (109 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectroscopic Studies, and Structure of an Unusual Dirhenium Complex with a Bridging Hydride Ligand

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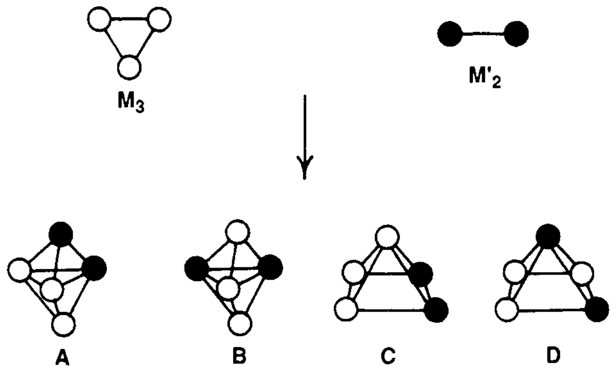
The preparation and characterization of an unusual dirhenium hydrido–carbonyl compound is described. The product has been accessed by several methods, including the reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with various carbonyl clusters in the presence of H_2 and the direct combination of the starting material with an H_2/CO gas mixture in refluxing toluene. Details of these and other syntheses are presented. Compound **1**, $Re_2(\mu\text{-Cl})(\mu\text{-H})Cl_2(CO)_2(dppm)_2$, crystallizes in the tetragonal space group $P4_12_12$ with unit cell dimensions $a = 14.935$ (2) Å, $b = 14.935$ (2) Å, $c = 25.804$ (2) Å, $V = 5755$ (4) Å^3, and $Z = 4$. The structure was refined to least-squares residuals of $R = 0.0304$, $R_w = 0.0368$ and quality-of-fit 0.643. The molecules reside on crystallographic 2-fold axes, and the asymmetric unit is defined by half of a formula unit. The binuclear structure consists of two trans diphosphine ligands bisecting an equatorial plane that contains one bridging and two terminal chloride ligands on the same side of the molecule as well as two terminal carbonyl ligands. The bridging hydride ligand, although not located in the X-ray refinement, is postulated on the basis of detailed ^1H NMR studies and is further substantiated by the diamagnetism of the compound. The μ-H resonance is quite unusual with a chemical shift of $\delta = +12.75$ ppm in CD_2Cl_2. The presence of the μ-H ligand leads to the formulation of **1** as a molecule possessing an Re_2^{4+} core with an edge-sharing bioctahedral geometry. Both the Re–Re distance of 2.605 (1) Å and the electrochemistry of the new compound ($E_{p,c} = +1.47$, $E_{1/2}(ox) = +0.63$, $E_{1/2}(red)_1 = -0.73$, and $E_{1/2}(red)_2 = -1.44$ V vs Ag/AgCl) are very similar to that which has been reported for other dirhenium M_2L_{10} systems containing a mixture of chloride, phosphine, and carbonyl ligands. This point is discussed along with other pertinent structural data. In addition to an X-ray study, the new compound was characterized by elemental analysis, infrared spectroscopy, FAB mass spectrometry, ^1H and ^{31}P NMR spectroscopy, and cyclic voltammetry.

We are currently investigating reactions between various coordinatively unsaturated binuclear compounds and trinuclear carbonyl complexes. In addition to the likelihood of formation of tetra- or pentanuclear mixed-metal clusters by this approach,[1-10] as in Scheme I, there is also a possibility that interesting homometallic products resulting from ligand exchange may be isolated.[11] In a recent paper by Shore and co-workers, the former result was realized in the case of the reaction between $(\mu\text{-H})_2Os_3(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_n]_2$ (n = 2, 3) under a hydrogen atmosphere to form $(\mu\text{-H})_2(\eta^5\text{-}C_5H_5)_2Mo_2Os_3(CO)_{12}$.[8] This novel pentanuclear cluster is derived from a formal addition of the Mo–Mo dimer to an edge of the Os_3 unit with retention of the Mo–Mo bond (structure B in Scheme I). This synthetic approach had previously been studied by Curtis and co-workers, but evidently no reaction occurred in the absence of H_2.[12]

Scheme I. Pentanuclear Cluster Frameworks Derived from Trinuclear (M_3) and Binuclear (M'_2) Fragments



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In this paper we describe our recent work in the chemistry of the triply bonded complex $Re_2Cl_4(dppm)_2$ with the carbonyl clusters $H_2Os_3(CO)_{10}$ and $M_3(CO)_{12}$ (M = Ru, Os) and with H_2/CO mixtures. All of these reactions produce the unusual μ-hydrido carbonyl species $Re_2(\mu\text{-}Cl)(\mu\text{-}H)Cl_2(CO)_2(dppm)_2$. In the cases where the group VIII clusters were used, this product is obviously a result of ligand migration reactions. This chemistry has been seen to dominate in other reactions between dimeric and trimeric complexes.[11] We have noted that the reaction between $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ and $Ru_3(CO)_{12}$ leads to the formation of $Ru_3(\mu\text{-}Cl)_2(CO)_8(P\text{-}n\text{-}Bu_3)_2$ as the major Ru-containing product.[11a] Others have reported that the reaction of $Fe_3(CO)_{12}$ with the cyclopentadienyliron dimer $[Cp(CO)Fe\{\mu\text{-}C(CF_3){=}C(CF_3)SMe\}_2Fe(CO)Cp]$ leads to an exchange of ligands and the formation of several new compounds.[11b] In the event that the products can be easily separated, ligand-transfer reactions are a useful route to compounds that cannot be prepared by direct reaction of the parent compounds with the particular ligand(s) involved.

Experimental Section

Starting Materials and Reaction Procedures. The starting materials $H_2Os_3(CO)_{10}$[13] and $Re_2Cl_4(dppm)_2$[14] were prepared according to published methods. The clusters $M_3(CO)_{12}$(M = Ru, Os) were purchased from Strem Chemicals and were used without further purification. Solvents were dried over sodium–potassium/benzophenone and distilled before use. Unless otherwise specified, all reactions were carried out under an argon atmosphere by using standard Schlenk-line techniques.

A. Synthesis of $Re_2(\mu\text{-}Cl)(\mu\text{-}H)Cl_2(CO)_2(\mu\text{-}dppm)_2$ (1). The following methods involve refluxing a toluene solution of $Re_2Cl_4(dppm)_2$ in the presence of various carbonyl clusters ($H_2Os_3(CO)_{10}$, $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$) with a constant flush of H_2 passing through the solution. Separation of the resulting mixtures was achieved by column chromatography.

(i) Reaction of $Re_2Cl_4(dppm)_2$ with $H_2Os_3(CO)_{10}$ in the Presence of H_2. A quantity of $H_2Os_3(CO)_{10}$ (0.10 g, 0.117 mmol) and $Re_2Cl_4(dppm)_2$ (0.15 g, 0.12 mmol) was placed in a 30-mL Schlenk tube equipped with a condenser and a stir bar. Toluene (20 mL) was added, and the solution was heated to reflux with a slow stream of H_2 bubbling through the solution. During the course of the reaction, the solution color changed from dark purple to brown-green. The progress of the reaction was monitored by infrared spectroscopy and was judged to be complete after 12 h on the basis of the disappearance of $H_2Os_3(CO)_{10}$. The solution was cooled to room temperature, and the solvent was removed to give a brown tar. Diethyl ether was added to extract a brown solution, leaving behind a dark green precipitate, which was chromatographed on a silica gel column using hexane/CH_2Cl_2 (1:3 v/v) as the eluent. The first 50-mL fraction came off the column as a colorless solution and contained a white compound, which was identifed as $H_4Os_4(CO)_{12}$ by a comparison of its infrared and ^1H NMR spectroscopy to that reported in the literature;[13] yield 0.05 g (39% based on $H_2Os_3(CO)_{10}$). IR (CH_2Cl_2): ν(CO) 2085 (m), 2067 (s), 2019 (s), 1995 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ −20.44 (s). Mass spectrum: parent ion, m/z = 1101.9 (^{192}Os).

The remainder of the chromatographed sample came off the column as a green band and contained the product $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ identified on the basis of spectroscopic and crystallographic data (vide infra); yield 0.10 g (70%). IR (CH_2Cl_2): ν(CO) 1898 (vs), 1864 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 12.75 (1 H, s), 7.35 (40 H, m), 4.70 (2 H, m), 4.27 (2 H, m). Mass spectrum: parent ion, m/z = 1304.5 (^{187}Re). Anal. Calcd for $C_{52}H_{45}Cl_3O_2P_4Re_2$: C, 47.87; H, 3.50. Found: C, 48.34; H, 4.10.

Attempts to purify the original diethyl ether extract by column chromatography or by recrystallization were unsuccessful.

(ii) Reaction of $Re_2Cl_4(dppm)_2$ with $Os_3(CO)_{12}$ in the Presence of H_2. A mixture of $Os_3(CO)_{12}$ (0.10 g 0.110 mmol) and $Re_2Cl_4(dppm)_2$ (0.14 g, 0.110 mmol) in toluene (20 mL) was refluxed with a constant slow stream of H_2 passing through the solution. The reaction was monitored by IR spectroscopy and was stopped after 8 h on the basis of the disappearance of $Os_3(CO)_{12}$.

The resulting solution was evaporated to dryness, and the residue was extracted with diethyl ether (3 × 20 mL) to give a brown solution, leaving behind a dark brown precipitate that was purified by column chromatography. Elution with hexane/CH_2Cl_2 (1:3 v/v) gave a colorless solution that contained 0.020 g of $H_4Os_4(CO)_{12}$ (yield ~20%) and a small amount of a green compound (0.015 g) that was characterized as $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ (yield ~10%). A brown, intractable material was retained at the top of the column. The IR, ^1H NMR, and mass spectral data for both compounds are given in section A(i) above.

(iii) Reaction of $Re_2Cl_4(dppm)_2$ with $Ru_3(CO)_{12}$ in the Presence of H_2. A mixture of $Ru_3(CO)_{12}$ (0.10 g, 0.156 mmol) and $Re_2Cl_4(dppm)_2$ (0.21 g, 0.16 mmol) in toluene (20 mL) was refluxed with a constant slow stream of H_2 bubbling through the solution. The reaction was monitored by IR spectroscopy and was stopped after 8 h on the basis of the disappearance of $Ru_3(CO)_{12}$.

The reaction solution was worked-up in the same manner as reaction A(ii). The main product that was isolated was $H_4Ru_4(CO)_{12}$ (yield 0.018 g (~15%);[13] IR (CH_2Cl_2) ν(CO) 2080 (s), 2066 (vs), 2022 (s), 2010 (w) cm^{-1}), along with a small amount of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ (yield <5%).

(iv) Reaction of $Re_2Cl_4(dppm)_2$ with an H_2/CO Gas Mixture. A solution of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.08 mmol) in toluene (20 mL) was refluxed for ca. 20 h with a rapid stream of H_2 and a slow stream of CO passing through the solution. The resulting cloudy green solution contained a small amount of olive green precipitate, which was collected by filtration and identified as $Re_2Cl_4(CO)_2(dppm)_2$ by its Nujol mull infrared spectrum[15] (ν(CO) 1958 (vs), 1946 (vs), 1722 (m) cm^{-1}); yield 0.011 g (17%). The green filtrate was reduced in volume to yield 0.050 g of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ characterized on the basis of infrared and ^1H NMR spectroscopy; yield 48%.

B. Reaction of $Re_2Cl_4(dppm)_2$ with $H_2Os_3(CO)_{10}$ in the Absence of H_2. The reaction was performed under conditions identical with those described in section A(i) but without the constant flush of H_2 through the solution. During the reaction, the solution color changed from dark purple to cloudy brown-green, and after 68 h of reflux, infrared spectroscopy indicated that very little $H_2Os_3(CO)_{10}$ remained. After removal of the solvent, the residue was extracted with diethyl ether (20 mL) and filtered to yield a brown precipitate and a brown solution. The brown solid was dissolved in THF (20 mL) and chilled to −10 °C to give a green solid which did not contain carbonyl ligands as judged by infrared spectroscopy. The nature of the compound is under further investigation. There was no evidence for the presence of the title compound in the remaining brown THF solution or the diethyl ether solution. The only identifiable ν(CO) band in these solutions may be attributed to the starting material $H_2Os_3(CO)_{10}$.

C. Reactions of $Re_2Cl_4(dppm)_2$ with Hydride Reducing Agents. (i) Reaction of $Re_2Cl_4(dppm)_2$ with $NaBH_4$ in the Presence of CO. A suspension of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.08 mmol) and $NaBH_4$ (0.003 g, 0.08 mmol) was refluxed in toluene (20 mL) for 3 h with a constant slow stream of CO passing through the solution. During this time, an olive green precipitate formed in the solution. It has been identified as $Re_2Cl_4(CO)_2(dppm)_2$.[15] IR (Nujol): ν(CO) 1958 (s), 1944 (s), 1721 (m) cm^{-1}.

The reaction was then continued after the addition of an excess amount of $NaBH_4$ (0.015 g, 0.4 mmol) into the suspension of $Re_2Cl_4(dppm)_2(CO)_2$ in toluene. The solution was stirred for 6 h to give a soluble green compound which exhibits a single ν(CO) stretch at 1857 cm^{-1}. Attempts to characterize the compound are underway.

(ii) Reaction of $Re_2Cl_4(dppm)_2$ with NaH in the Presence of CO. A mixture of $Re_2Cl_4(dppm)_2$ (0.10 g, 0.08 mmol) and NaH (0.002 g, 0.08 mmol) was refluxed in CH_2Cl_2 (20 ml) for 24 h with a constant slow stream of CO passing through the solution. An infrared spectrum of the resulting yellow-green solution revealed that the product is $Re_2Cl_4(CO)_2(dppm)_2$.

A further reaction was carried out by the addition of an excess amount of NaH (0.01 g, 0.4 mmol) into the reaction solution containing $Re_2Cl_4(CO)_2(dppm)_2$. The solution was stirred for 24 h to give a dark green solution which exhibits a complicated ν(CO) region. IR (CH_2Cl_2): 1955 (s), 1945 (s), 1925 (s), 1845 (m), and 1724 (m) cm^{-1}. There was no evidence for the formation of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ in this reaction.

Physical Measurements. Electrochemical measurements were carried out by using an EG&G Princeton Applied Research Model 362 scanning potentiostat in conjunction with a BAS Model RXY recorder. Cyclic voltammetry was carried out at 22 ± 2 °C in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode and are uncorrected for junction potentials. ^1H NMR spectra were obtained on a WM250 Brucker spectrometer with an ASPECT 3000 computer. $^{31}P\{^1H\}$ NMR spectra

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Table I. Summary of Crystallographic Parameters for $Re_2Cl_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_2(\mu\text{-}dppm)_2$

formula	$Re_2Cl_3P_4O_2C_{52}H_{45}$	Z	4
fw	1304.59	d_{calc}, g/cm^3	1.545
space group	$P4_12_12$	μ(Mo Kα), cm^{-1}	45.9
a, Å	14.935 (2)	radiation (graphite-monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
b, Å	14.935 (2)		
c, Å	25.804 (7)		
α, deg	90	temp, °C	22 ± 2
β, deg	90	R^a	0.0304
γ, deg	90	R_w^b	0.0368
V, Å^3	5755 (4)		

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

were recorded on a 180-MHz Brucker spectrometer with an internal deuterium lock and 85% H_3PO_4 as an external standard. Infrared spectra were recorded on a Perkin-Elmer 599 or a Nicolet 740 FT-IR spectrophotometer. Fast atom bombardment (FAB) mass spectrometry studies were performed on a JEOL HX 110 double-focusing mass spectrometer housed in the National Institutes of Health/Michigan State University Mass Spectrometry Facility; the sample was dissolved in a 3-nitrobenzyl alcohol matrix.

X-ray Crystal Structure Determination of $Re_2Cl_2(\mu\text{-}H)(\mu\text{-}Cl)(CO)_2(dppm)_2$. A. Data Collection and Reduction. The structure of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ (**1**) was determined by general procedures that have been fully described elsewhere.[16] A green crystal of dimension 0.40 × 0.30 × 0.25 mm was covered with epoxy cement and mounted at the end of a glass fiber. Geometric and intensity data were obtained on a Nicolet P3/F diffractometer equipped with graphite-monochromated Mo Kα radiation. A rotation photograph indicated that the crystal diffracted well. An automatic search routine was used to locate 25 reflections in the range $20 < 2\theta < 30°$. The reduced cell dimensions indicated that the crystal belongs to the tetragonal crystal system; axial photographs revealed that the Laue class is 4/*mmm*.

Data reduction was carried out by standard methods with use of well-established computational procedures.[17] Systematic absences from the data led to the space group choices of $P4_12_12$ and $P4_32_12$. A θ–2θ motion was used to scan 8125 data points in a range of $4.5 \leq 2\theta \leq 45$. The structure factors were obtained after Lorentz and polarization corrections. During intensity-data collection three check reflections were measured at regular intervals; an average 4.8% loss in intensity was observed. The program CHORT was applied to correct for this. Azimuthal scans of reflections with Eulerian angle χ near 90° (3 curves) were used as a basis for an empirical absorption correction. After averaging of the equivalent reflections, there remained 4834 unique data and 3319 reflections with $F_o^2 \geq 3\sigma(F_o)^2$.

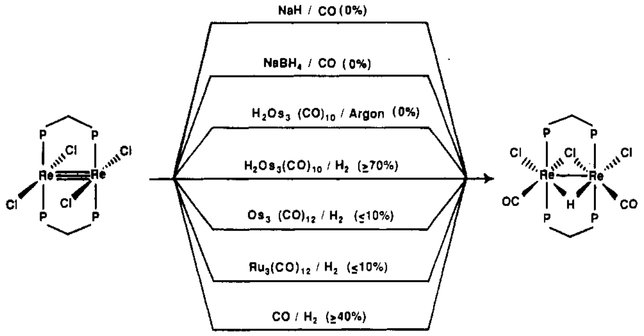
B. Structure Solution and Refinement. The position of the unique Re atom was obtained by the application of MULTAN 11/82. A sequence of successive difference Fourier maps and least-squares cycles led to full development of the coordination sphere. The final full-matrix refinement involved 289 variable parameters and 3319 data, for a data-to-parameter ratio of 11.5. The refinement converged with residuals of $R = 0.0304$, $R_w = 0.0368$ and quality-of-fit 0.643. A comparison of the refinement in the two enantiomorphs revealed that $P4_12_12$ is the correct choice for the space group. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Complete tables of positional parameters, bond distances and angles, anisotropic thermal parameters, and structure factors are available as supplementary material.

Results and Discussion

A. Synthetic Methods. Although our initial goal of isolating a heterometallic product from the reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with the coordinatively and electronically unsaturated $Re_2Cl_4(dppm)_2$ was not realized, we were intrigued by the chemistry that resulted in the formation of the unusual dicarbonyl(μ-hydrido)dirhenium complex (**1**). We pursued the project by systematically examining various factors that would be expected to influence the yield of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$.

The source of the hydride ligand in our original synthesis of $Re_2(\mu\text{-}Cl)(\mu\text{-}H)Cl_2(CO)_2(dppm)_2$ is of considerable interest to us in this work. According to some published reports, the hydride ligand may be derived from $H_2Os_3(CO)_{10}$ from metal hydride coupling,[18] followed by H–Os bond scission, chemistry that has been exploited for the preparation of heterometallic cluster compounds.[1-9,19] In order to determine the importance of $H_2Os_3(CO)_{10}$ as the source of the hydrogen atom in our original serendipitous synthesis of **1**, several additional reactions were carried out. In one approach we used $Os_3(CO)_{12}$ instead of $H_2Os_3(CO)_{10}$ as the cluster starting material (see section A(ii) in the Experimental Section). In the presence of H_2 gas the reaction produces $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$, although in a very low yield (5–10%). This rules out the possibility that the *major* reaction pathway is through initial formation of $H_2Os_3(CO)_{10}$ from the reaction of H_2 and $Os_3(CO)_{12}$, which is known to be facile, followed by a slower reaction of $H_2Os_3(CO)_{10}$ with $Re_2Cl_4(dppm)_2$. If this were the case, one would expect a yield that is comparable to that obtained when starting directly from $H_2Os_3(CO)_{10}$ (~70%). Furthermore, in the chemistry involving $Ru_3(CO)_{12}$, section A(iii), there is no analogous triruthenium dihydride complex which could act as an intermediate, yet one still obtains a small amount of **1**.

Scheme II. Attempted Synthetic Routes and Approximate Yields for the Synthesis of $Re_2(\mu\text{-}Cl)(\mu\text{-}H)Cl_2(CO)_2(dppm)_2$



It is important to note that if the reaction between $H_2Os_3(CO)_{10}$ and $Re_2Cl_4(dppm)_2$ is performed under an atmosphere of argon instead of hydrogen, the resulting reaction solution contains a mixture of products including the osmium starting material and an intractable brown compound but none of the title compound. This result taken together with the above observations suggests that the presence of H_2 facilitates the reaction, presumably by assisting in the formation of an intermediate(s).

Several additional approaches aimed at the rational synthesis of **1** included reactions of $Re_2Cl_4(dppm)_2$ under a CO atmosphere with sodium borohydride and sodium hydride, sections C(i) and C, (ii). These reactions led to product mixtures that do not contain the title compound as determined by infrared and ^1H NMR spectroscopy. The details of this chemistry will be discussed at a later date.

We now turn to the most interesting and useful result obtained in this work. Namely, the successful synthesis of the title compound by a direct reaction of $Re_2Cl_4(dppm)_2$ with an H_2/CO gas mixture at atmospheric pressure, section A(iv). The yield of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ by this method is typically between 50 and 80%, depending on the relative concentrations of H_2 and CO in the reaction. If the CO concentration is in excess, one obtains a high yield of the previously reported compound $Re_2Cl_4(CO)_2(dppm)_2$ but very little of **1**. This result clearly demonstrates that a hydrido-cluster intermediate is not an essential requirement in the formation of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$.

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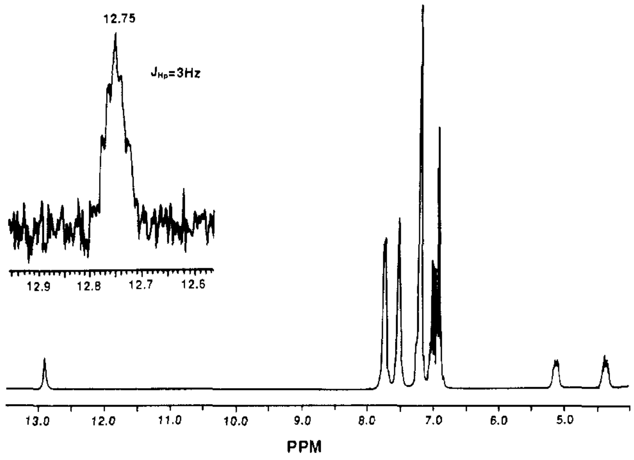

Figure 1. ^{1}H NMR spectrum of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ in CD_2Cl_2 at 22 °C. The inset shows the hydride resonance at $\delta = +12.75$ after decoupling the methylene protons at $\delta = +4.7$ and $+4.2$ ppm.

Of course we do not rule out the idea that a hydride-coupling reaction is one possible pathway in the chemistry involving the clusters $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $M_3(CO)_{12}$ (M = Ru, Os). The synthetic routes into $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ that were investigated in this work are summarized in Scheme II.

From the aforementioned discussion it can be ascertained that the source of CO ligand in these reactions is not particularly important in determining the yield of **1** but that the presence of molecular hydrogen is a requirement—even in the reaction starting from $(\mu\text{-}H)_2Os_3(CO)_{10}$. The general importance of this finding lies in its implications for future research involving reactions of H_2 with multiple M–M bonds, chemistry that has not been explored to a great extent.[20] Actually, we have examined the reaction of H_2 with $Re_2Cl_4(dppm)_2$ under the same experimental conditions (1 atm H_2, 110 °C). A reaction occurs within 12 h to yield a dark olive green solid. The possibility that this product is a hydride intermediate in the chemistry leading to $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ is currently under investigation.

(i) NMR Spectroscopy. The observation of sharp signals in the ^{1}H NMR spectrum supports the formulation of the compound as a diamagnetic Re_2^{4+} species and not a paramagnetic complex derived from an Re_2^{3+} core. The diamagnetism was further demonstrated by a magnetic susceptibility measurement that was carried out in solution by the Evans method.[21] The absence of a shifted solvent resonance rules out the presence of a paramagnetic species. A room-temperature ^{1}H NMR spectrum of **1** in CD_2Cl_2 (Figure 1) consists of the phenyl proton resonances as a multiplet centered at $\delta = 7.5$ ppm, the methylene resonances of the dppm located at $\delta = 4.70$ and 4.27 ppm, which approximates to an ABX_4 pattern, and surprisingly, a broad resonance at $\delta = 12.75$ ppm, which integrates as one proton. As the reproducibility of the latter signal for several different samples of **1** was excellent, we conclude that the resonance is due to a hydride ligand in the compound and not to some anomalous impurity. Indeed, the X-ray structure (vide supra) of **1** reveals an open bridging site where a hydrogen atom may be expected to reside. It should be noted that unusual downfield chemical shifts have been reported for other hydrido-bridged metal–metal-bonded dimers of the early transition metals. For example, the hydride resonances of $NaW_2(\mu\text{-}H)(OR)_8$(R = *i*-Pr, CH_2-*t*-Bu) appear as sharp singlets ca. $\delta = +9$ ppm[22] and the chemical shift of the μ-H groups for $Ta_2Cl_6(PMe_3)_4(\mu\text{-}H)_2$ occurs at $\delta = +8.52$ ppm.[23] To the best of our knowledge, however, the value of +12.75 ppm is the most deshielded hydride ligand that has been reported to date. The unusual chemical shift of the bridging hydride is probably due to the diamagnetic anisotropy of the multiple metal–metal bond.[24]

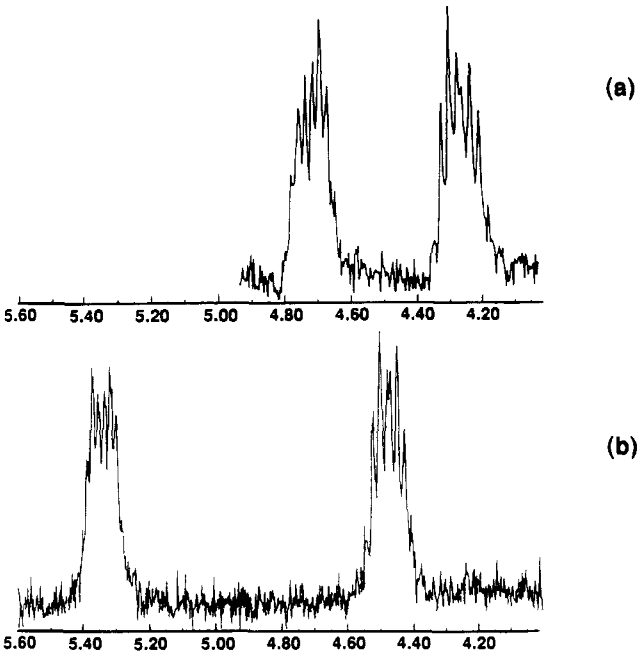

Figure 2. ^{1}H NMR spectra at 22 °C of the dppm methylene protons of compound **1** in (a) CD_2Cl_2 and (b) acetone-d_6.

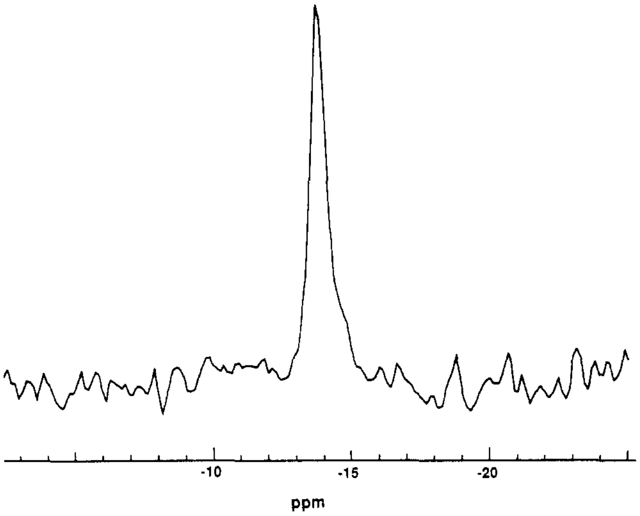

Figure 3. The undecoupled ^{31}P NMR spectrum of **1** in CD_2Cl_2 at 22 °C.

The presence of the bridging hydride ligand was further confirmed by selective decoupling experiments. As shown in Figure 1, when the methylene resonances of the dppm ligand are decoupled, a symmetrical quintet is observed for the signal at $\delta = +12.75$ ppm ($J_{P\text{-}H} = 3$ Hz) due to virtual coupling to the four trans phosphorus atoms, which are symmetrically situated with respect to the bridging hydride. Furthermore, when the resonance at $\delta = 12.75$ ppm is decoupled, both sets of methylene resonances are affected, thereby establishing that it is not an NOE effect but a through-bound coupling phenomenon. If an NOE effect were responsible, only one methylene proton (the one closest to the bridging hydride) would be affected.

We have also observed a solvent effect on the ^{1}H NMR spectrum of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$. The methylene resonances, which exhibit a closely spaced ABX_4 pattern in

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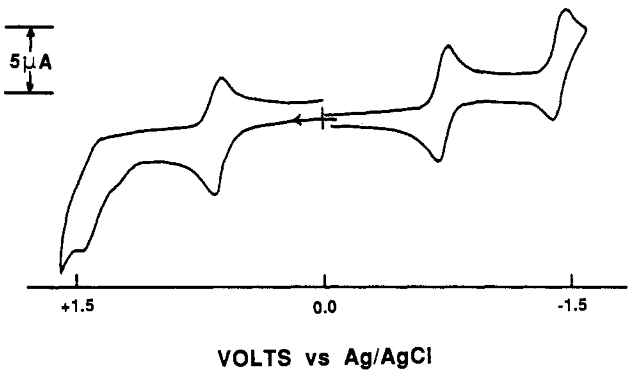

Figure 4. Cyclic voltammogram of **1** in 0.2 M TBAH–dichloromethane at 200 mV/s at a Pt-disk electrode.

CD_2Cl_2, appear as an AM pattern (δ = 4.47, 5.35 ppm) with superimposed phosphorus coupling in acetone-d_6 (Figure 2). Also, the chemical shift of the μ-H ligand is different in the two oxygen-donor solvents. In acetone-d_6 and THF-d_8, the μ-H resonance occurs at δ = +12.89 and +12.91 ppm, respectively. These observations are consistent with the formation of a weakly solvated $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ species. The ν(CO) bands are also solvent-dependent (IR (acetone): ν(CO) 1868 (vs), 1901 (s) cm^{-1}), which further supports the notion that oxygen donors are capable of interacting with the complex.

A room-temperature ^{31}P spectrum in CD_2Cl_2 displays a singlet at δ = −14 ppm, which is shifted downfield from free dppm (δ = 22.7 ppm) as expected (Figure 3). The broad nature of the signal is due to the unresolved coupling to the dppm methylene protons and to the bridging hydride.

Finally, the T_1 relaxation time of the hydride resonance was measured in order to examine the possibility of the presence of molecular hydrogen in the compound as well as to make a comparison to those values reported for other hydride compounds. The value of 343 (62) ms at 22 °C is 1 order of magnitude greater than those expected for a dihydrogen ligand.[25] In keeping with the ^1H NMR spectrum of the compound in which the hydride signal appears as a quintet rather than a broad, featureless resonance as is typical for η^2-H_2 ligands, it is unlikely that a molecular hydrogen ligand is present.

(ii) Mass Spectrometry. An analysis of **1** by positive fast atom bombardment (FAB) mass spectrometry gave a spectrum with well-resolved peaks. In order to further substantiate that the highest mass peak at m/z = 1304.5 corresponding to $C_{52}H_{45}Cl_3O_2P_4Re_2$ is due to the molecular ion (M^+) rather than the pseudo molecular ion $(M + H)^+$, the related compound $Re_2Cl_4(CO)_2(dppm)_2$ has been examined by the same technique. The highest mass peak of this sample (m/z = 1339; ^{187}Re) corresponded to the correct molecular formula, i.e. to M^+ and not to $(M + H)^+$. It is reasonable to expect that very similar compounds will exhibit analogous behavior under identical FAB–MS experimental conditions. This analysis combined with the NMR data (vide supra) strongly supports the presence of the hydride ligand.

B. Electrochemistry. The new compound exhibits a rich electrochemistry, as evidenced by the presence of four redox processes between +2.0 and −2.0 V. The cyclic voltammogram of the complex $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ in 0.2 M TBAH–CH_2Cl_2 exhibits two reversible processes at $E_{1/2}$ = −0.73 V and $E_{1/2}$ = −1.44 V vs Ag/AgCl, which correspond to two one-electron reductions of the compound, a reversible oxidation at $E_{1/2}$ = +0.63 V vs Ag/AgCl, and an irreversible oxidation near the solvent limit at $E_{p,a}$ = +1.47 V (Figure 4). This extensive redox behavior is characteristic of edge-sharing bioctahedral dirhenium complexes and resembles that which was reported for $Re_2Cl_6(dppm)_2$,[26] $Re_2Cl_6(Ph_2Ppy)_2$,[26] $Re_2Cl_4(CO)_2(dppm)_2$,[15] and $Re_2Cl_4(\mu\text{-}SePh)_2(dppm)_2$.[27]

Table II. Selected Bond Distances (Å) and Angles (deg) for $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ (**1**)

	Distances		
Re(1)–Re(1)	2.605 (0)	P(2)–C(2)′	1.846 (6)
Re(1)–Cl(1)	2.526 (3)	P(2)–C(31)	1.840 (7)
Re(1)′–Cl(1)	2.525 (1)	P(2)–C(41)	1.843 (8)
Re(1)–Cl(2)	2.449 (2)	O(1)–C(1)	1.112 (12)
Re(1)–P(1)	2.464 (2)	C(11)–C(12)	1.381 (11)
Re(1)–P(2)	2.446 (2)	C(11)–C(16)	1.404 (13)
P(1)–C(2)	1.833 (8)	C(14)–C(15)	1.372 (14)
P(1)–C(11)	1.832 (7)	C(15)–C(16)	1.430 (11)
P(1)–C(21)	1.847 (8)		
	Angles		
Re(1)′–Re(1)–Cl(1)	58.93 (1)	Re(1)′–Re(1)–C(1)	112.2 (3)
Re(1)′–Re(1)–Cl(2)	146.23 (5)	Cl(1)–Re(1)–C(1)	170.2 (3)
Re(1)′–Re(1)–P(1)	95.81 (4)	Cl(2)–Re(1)–C(1)	101.4 (3)
Cl(1)–Re(1)–Cl(2)	87.76 (5)	Re(1)–P(1)–C(2)	105.2 (2)
Re(1)′–Cl(1)–Re(1)	62.11 (5)	Re(1)–C(1)–O(1)	175.9 (8)

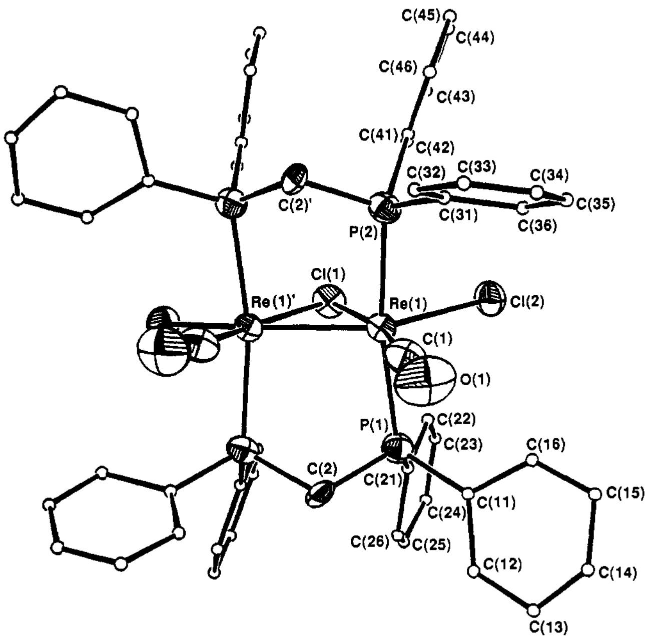

Figure 5. ORTEP drawing of a single molecule of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$, showing the atom-labeling scheme. The hydrogen atom was not located crystallographically. Phenyl group carbon atoms in the dppm ligands are represented as small circles for clarity. All other atoms are represented by their 50% probability ellipsoids.

C. Crystal Structure of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ (1). The important bond distances and angles for **1** are given in Table II. All other information pertaining to the refinement can be found in the supplementary material. An ORTEP plot of the molecular structure with the atom-labeling scheme is shown in Figure 5. The bridging hydrogen atom was not located; thus, it does not appear in the plot.

The structure of the dinuclear complex consists of two trans diphosphine ligands bisecting a plane containing the rhenium atoms, two cis terminal CO groups, and the three chloride ligands. The structure is similar to those found for other carbonyl complexes of the $Re_2(dppm)_2^{4+}$ unit in that the π-acceptor ligands are situated on the same side of the molecule.[28] Also, the conformation of the Re–P–C–P–Re five-membered ring formed by the metal atoms and the dppm ligand is that of a half-chair with the two methylene carbon atoms in a syn rather than anti configuration, in keeping with the 2-fold symmetry of the molecule (Figure 6). As in previously characterized dirhenium complexes containing CO or CNR ligands, the bridgehead carbon atoms are folded to the side of the molecule containing the π-acceptor ligands.[28] This syn structure is preserved in solution, as evidenced

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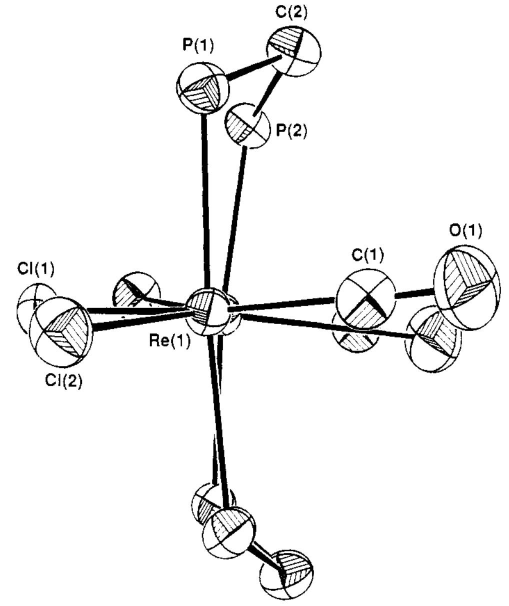

Figure 6. A side view of a molecule of **1**, emphasizing the syn orientation of the methylene bridgehead carbon atoms. The degree of twist from the perfectly eclipsed conformation is 8.5°.

by the ^1H NMR spectrum in the $-CH_2-$ regions of the dppm ligands (vide supra). As the side view of the molecule in Figure 6 clearly shows, the diphosphine ligands are twisted from an eclipsed conformation ($\chi = 8.5°$), resulting in a molecular symmetry of C_2 rather than C_{2v}.

The distances and angles in the molecule are within expected ranges (Table II). The metric parameters for **1** are very similar to those exhibited by other edge-sharing bioctahedral molecules such as $Re_2Cl_6(dppm)_2$[26] and $Re_2Cl_4(CO)_2(dppm)_2$[15] with the exception that the carbonyl ligands are not as swept back from the center of the molecule as is ordinarily the case with terminal ligands. In $Re_2Cl_4(CO)_2(dppm)_2$, the Re–Re–C_t angle is 125 (2)° and Re–Re–Cl_t = 141.3 (7)°.[15] In the present molecule, Re–Re′–C_t = 112.2 (3)° and Re–Re′–Cl_t = 146.23 (5)°. The unusually small angle that the CO ligands in **1** assume with respect to the metal–metal bond axis suggests that some attractive interaction may be occurring with the bridging hydride ligand. Attempts are underway to study the reactivity of the μ-H ligand with respect to CO activation.

The Re–Re bond length of 2.605 (1) Å is quite long for a complex formally derived from the Re_2^{4+} core. In fact this distance is close to those values found in Re_2^{6+} compounds such as $Re_2Cl_6(dppm)_2$ (Re–Re = 2.616 (1) Å).[26] The long metal–metal distance in $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ is even more surprising considering that it contains a μ-H group, which is known to have the effect of drawing metal atoms closer together. Clearly, more examples of these types of carbonyl–hydrido dimers are required to explain the structural parameters of this molecule.

Conclusion

The studies described herein were undertaken to gain a more complete understanding of the formation of an unusual hydrido–dirhenium complex. We have verified that the compound $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ can be prepared by reactions of $Re_2Cl_4(dppm)_2$ with carbonyl clusters under an H_2 atmosphere and by the direct reaction of $Re_2Cl_4(dppm)_2$ with a CO/H_2 gas mixture at atmospheric pressure. The role of $H_2Os_3(CO)_{10}$ as a cluster precursor appears to be an important one in the high-yield synthesis of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$. We have also noted the behavior of H_2 in assisting the reaction to form the title compound. Attempts to stabilize reactive intermediates that might provide an interesting mixed-metal complex are still under investigation.

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Supplementary Material Available: Tables of crystallographic parameters, atomic positional and thermal parameters, full bond distances and angles, and anisotropic thermal parameters (7 pages); a listing of structure factors (37 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2\cdot CH_3C_6H_5$

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The $^3(d\sigma^*p\sigma)$ excited state of $Ir_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) reacts with hydrogen atom donors to give $Ir_2(TMB)_4H_2^{2+}$ (Ir_2H_2). This d^7–d^7 dihydride has been isolated as a tetraphenylborate salt: ν(Ir–H) 1940 cm^{-1}, ν(Ir–Ir) 136 cm^{-1}. $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2\cdot CH_3C_6H_5$, $Ir_2C_{95}H_{114}N_8B_2$, crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14), with $a = 10.54$ (2) Å, $b = 31.02$ (4) Å, and $c = 27.05$ (4) Å, $\beta = 91.57$ (3)°, $V = 8841$ (3) $Å^3$, and $Z = 4$. The Ir–Ir separation is 2.920 (2) Å, approximately 0.3 Å shorter than Ir–Ir in the d^8 dimer (Ir_2) but ~0.1 Å longer than in the diiodide, $Ir_2(TMB)_4I_2^{2+}$. The reaction of Ir_2H_2 with styrene gives Ir_2 and ethylbenzene.

Triplet $d\sigma^*p\sigma$ excited states of binuclear d^8 complexes abstract hydrogen atoms from a variety of organic and organometallic molecules.[1-6] In the case of $Pt_2(P_2O_5H_2)_4^{4-}$ (Pt_2), the inorganic product is $Pt_2(P_2O_5H_2)_4H_2^{4-}$ (Pt_2H_2); this dihydride has been characterized spectroscopically, but it has not been isolated in crystalline form.[6]

We have found that irradiation of $Ir_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) in the presence of 1,4-

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