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Reductive coupling of diisopropylcarbodiimide by a dirhenium carbonyl complex

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ABSTRACT

The reaction of $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$ with *N,N′*-diisopropylcarbodiimide yielded the new rhenium diamidinate complex $[Re(CO)_4]_2[(\mu\text{-}C_2(N\{iPr\})_4]$, **2**, in 59% yield that was formed by the reductive coupling of two of carbodiimide molecules at the central carbon atom. The diamidinate ligand is nonplanar and four iminyl nitrogen atoms are coordinated to two $Re(CO)_4$ groups in two chelating groups that have formed five-membered rings. Density functional molecular orbital analyses were used to explain the bonding of the diamidinate ligand to the two rhenium atoms. A second product $Re_2(CO)_8(\mu\text{-}OH)(\mu\text{-}H)$, **3** was obtained from the reaction of *N,N′*-diisopropylcarbodiimide and $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1**. Compound **3** was subsequently found to be a product of the reaction of **1** with traces of H_2O in the original reaction and was independently obtained in 60% yield from the reaction of **1** with H_2O. Compound **3** contains a bridging hydroxo ligand and a bridging hydrido ligand across the Re–Re bond between two mutually bonded $Re(CO)_4$ groups. Both new compounds were characterized structurally by single-crystal X-ray diffraction analysis.

1. Introduction

The metal-assisted reductive coupling of heteroallenes by C–C bond formation can lead to a variety of tetrasubstituted C_2-products ranging from oxalate from CO_2 [1] to diamidinates [2], oxamides [3] and ethylenetetrathiolates [4] from carbodiimides, isocyanates and carbon disulfide, respectively. The formation of oxalates by the C–C coupling of two equivalents of CO_2 could become an important route for recycling this major greenhouse gas and the reduction of oxalates could lead to useful C_2-organic compounds [5].

Tetrasubstituted C_2-products can serve as excellent ligands [1–4]. They invariably chelate to two metal atoms. Two coordination modes **A** or **B** have been observed depending on which pairs of the donor atoms **E** are coordinated to the metal atoms (Scheme 1).

In recent studies, we have been investigating the reactivity of dirhenium complexes $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$ [6] and $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}C_6H_5)$, **1**, [7] with aryl-gold compounds [7], arenes [8] and heteroarenes [9]. These reactions proceed by facile reductive elimination of 1-hexene and benzene, respectively and are accompanied by oxidative addition of C–Au and C–H bonds to the remnant dirhenium carbonyl grouping.

We have now extended our studies of the reactions of $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$ and **1** to include their reactions with N,N'diisopropylcarbodiimide and water. The results of these studies are reported herein.

2. Results and discussion

$Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$ with *N,N′*-diisopropylcarbodiimide in a solution in heptane heated to reflux for 25 min provided the new compound $[Re(CO)_4]_2[(\mu\text{-}C_2(N\{iPr\})_4]$, **2**, in 59% yield. Compound **2** was characterized by IR and ^1H NMR spectroscopy, mass spectrometry and single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **2** is shown in Fig. 1. Compound **2** contains a diamidinate ligand formed by a C–C reductive coupling of two *N,N′*-diisopropylcarbodiimide molecules. Two $Re(CO)_4$ groups bridge the diamidinate ligand in the 1,4-coordination mode **A** to form two chelating five-membered rings on opposite sides of the ligand. There is a twist in C_2N_4 group at the C1–C2 bond which gives the molecule and overall D_2-type symmetry. The dihedral angle between the two planes C2–C1–N4–N1and C1–C2–N2–N3 is 31.6°, see Fig. S1, but the eight methyl groups on the four *i*-Pr groups are equivalent by ^1H

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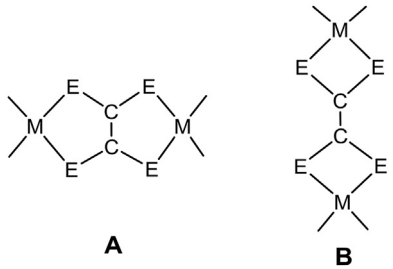


Scheme 1. Representations of the two common bonding modes of C–C reductively coupled heteroallenes in dinuclear metal complexes, E = O, S or NR.

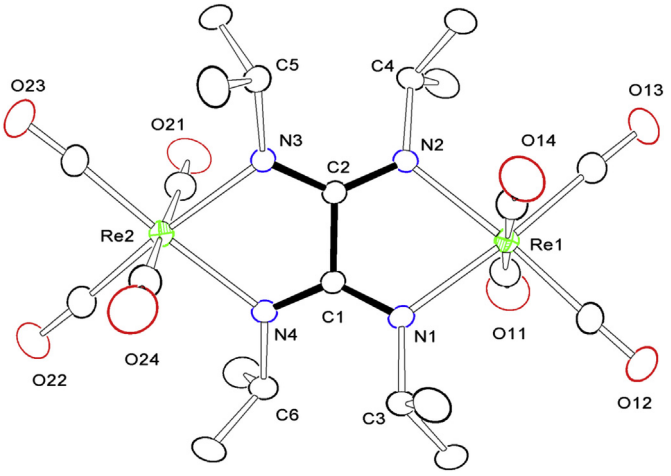
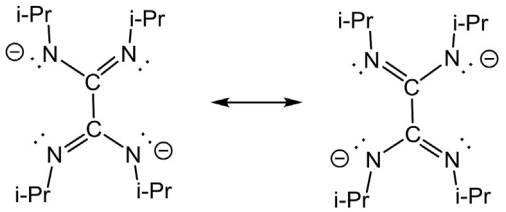


Fig. 1. The ORTEP diagram of the molecular structure of $[Re(CO)_4]_2[(\mu\text{-}C_2(N\{i\text{-}Pr\})_4]$, **2**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Re(1)–N(2) = 2.170(4), Re(1)–N(1) = 2.176(4), Re(2)–N(3) = 2.180(4), Re(2)–N(4) = 2.183(4), N(1)–C(1) = 1.330(6), N(1)–C(3) = 1.496(6), N(2)–C(2) = 1.323(6), N(2)–C(4) = 1.485(6), N(3)–C(2) = 1.332(6), N(3)–C(5) = 1.486(7), N(4)–C(1) = 1.335(6), N(4)–C(6) = 1.489(6) and C(1)–C(2) = 1.497(6).

NMR spectroscopy, $\delta = 1.10$ (d, $^3J_{H\text{-}H} = 6.3$ Hz) indicating that the C_2N_4 group must be twisting back and forth between the two equivalent nonplanar geometries on the NMR timescale at room temperature by rotational oscillations along the C1 – C2 bond. The C(1)–C(2) bond distance of 1.497(6) Å is only slightly shorter than that of a C–C single bond and thus any rotational barrier along this bond should be very small. The C–N distances to the atoms C1 and C2 are short, C1 – N1 = 1.330(6) Å, C1–N4 = 1.335(6), C2–N2 = 1.323(6) Å, C(2)-N3 = 1.332(6) Å, and are indicative of considerable C–N double bond character. A number of years ago, Floriani reported a similarly coordinated, tetra(tolyl)diamidinate ligand formed by the reductive coupling of two molecules of N,N′-di-ditolylcarbodimide in the bis-Cp_2Ti complex $(Cp_2Ti)_2[(\mu\text{-}C_2(N\{p\text{-}tolyl\})_4]$ [2a]. The C–C and C–N distances in that complex are very similar, 1.504(6) Å, 1.328(2) Å and 1.333(3) Å, to those in **2**. The nature of the C–N bonding in **2** was established by performing ADF DFT molecular orbital calculations, see below. The four Re–N distances, Re(1)–N(2) = 2.170(4) Å, Re(1)–N(1) = 2.176(4) Å, Re(2)–N(3) = 2.180(4) Å, Re(2)–N(4) = 2.183(4) Å are equal within experimental error. The rhenium atoms have a pseudo-octahedral 6-coordinate geometry.

To a first approximation, the diamidinate ligand can be viewed as a dianion and the bonding could be represented as an average of the two equivalent resonance structures shown in Scheme 2. The ligand is formally coordinated to two $Re(CO)_4$ monocations and each $Re(CO)_4$ group achieves an 18 electron configuration.



Scheme 2. Two resonance structures for the diamidinate ligand found in compound **2**.

To delve deeper into the bonding within the diamidinate ligand, ADF DFT molecular orbital calculations were performed at the PBEsol D3 level. Each C and N atom is planar and can be regarded as sp^2-hybridized. The π-bonding in the diamidinate ligand is the key to understanding the bonding in this ligand. The π-bonding can be represented by symmetry-adapted linear combinations (SALCs) of the six p-orbitals that lie perpendicular to the planes of each of the six atoms, i.e. the two central carbon atoms and the four nitrogen atoms. Chemdraw representations of these six SALCs together with each of their most closely related DFT MOs are shown in Fig. 2. Four of these MOs are bonding, the HOMO, HOMO-1, HOMO-10 and the HOMO-27 and are filled and two are antibonding, LUMO+23 and LUMO+4 and they are empty. The HOMO and HOMO-1 are essentially nonbonding within the C_2N_4 ligand. The HOMO-10 contains significant π-bonding across both *N*–C–N groups and this orbital accounts for the shortness of the C–N bonds in both of these groups. The HOMO-27 is important because it is the only one that contains a significant π-bonding interaction between the two carbon atoms C1 and C2. It is this supplemental π-bonding interaction between these two atoms that accounts for the shortening, albiet small, of the C1 – C2 bond relative to that of a traditional C–C single bond, see above. The weakness of the C–C bond allows a nonplanarity of the diamidinate ligand to develop which may relieve steric strain between the proximate isopropyl groups on the nitrogen atoms. Compound **2** was also formed in the reaction of **1** with *N*,*N*′-diisopropylcarbodiimide, but the only product that was isolated by TLC workup from this reaction was the new compound $Re_2(CO)_8(\mu\text{-}OH)(\mu\text{-}H)$, **3** which was subsequently obtained in a much better yield through an independent reaction of **1** with H_2O itself, see below.

The reaction of **1** with *N*,*N*′-diisopropylcarbodiimide in the presence of small amounts of water provided the new compound $Re_2(CO)_8(\mu\text{-}OH)(\mu\text{-}H)$, **3**, 28% yield, under typical reaction conditions, but compound **3** was subsequently obtained in a much better yield (60%) from the reaction of **1** with H_2O in the absence of *N*,*N*′-diisopropylcarbodiimide by heating to 40 °C for 24 h. It is quite likely that the *N*,*N*′-diisopropylcarbodiimide played no role in the formation of the **3** in the first reaction. Compound **3** was characterized by IR and ^1H NMR spectroscopy, mass spectrometry and single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **3** is shown in Fig. 3. Compound **3** contains two mutually-bonded $Re(CO)_4$ groups that contain both a bridging hydrido ligand and a bridging OH ligand across the Re–Re bond. The Re–Re bond is single and the distance, 3.0166(3) Å, is only slightly shorter than the Re–Re distance, 3.041(1) Å, found in $Re_2(CO)_{10}$ which contains an unsupported Re–Re single bond [10]. The Re–O distances to the bridging OH ligand are Re(1)–O(9) = 2.161(5) Å, Re(2)–O(9) = 2.151(5) Å, and are similar to the Re–O distances, 2.177(5) Å and 2.160(5) Å, observed in the related OH bridged dppm dirhenium carbonyl complex $Re_2(CO)_6(dppm)(\mu\text{-}OH)(\mu\text{-}H)$, dppm = 1,2-bis(diphenylphosphino)methane that was reported by Brown a number of years ago [11]. The bridging hydrido ligand in **3** was located and refined in the analysis of **3**, Re(1)–H(12) = 1.81(4) Å and Re(2)–H(1) = 1.81(4) Å. It resonates

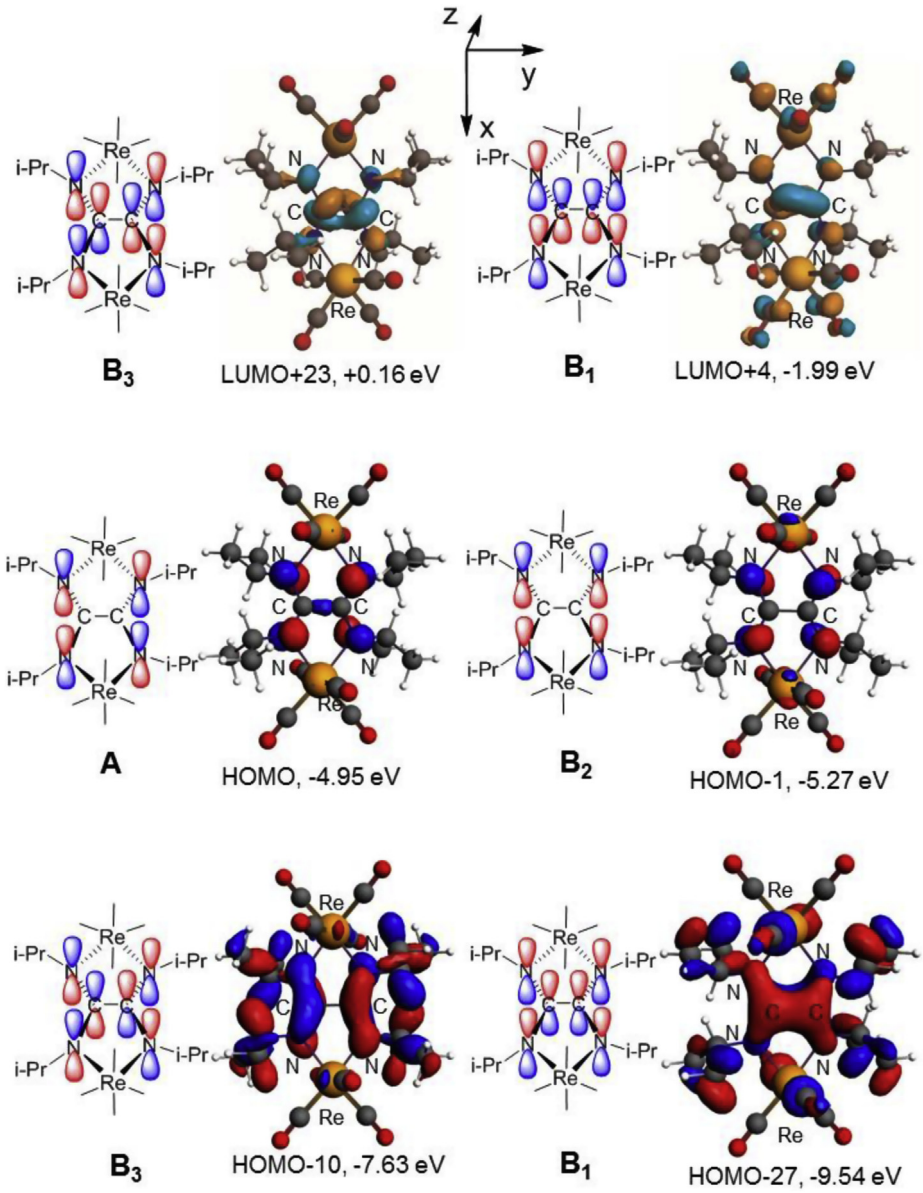


Fig. 2. Representations of the six π-molecular orbitals of the $C_2(Ni{-}Pr_4)$ ligand in **2**. On the left side is a Chemdraw view of the symmetry adapted linear combinations of p-orbitals derived by using D_2 symmetry. The most closely related ADF DFT MO is shown next to that on its right side, ISOvalue = 0.04.

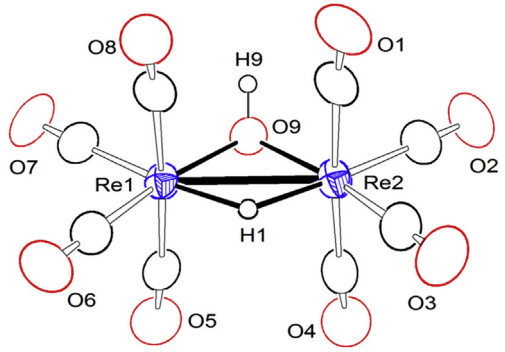


Fig. 3. The ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}OH)(\mu\text{-}H)$, **3**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Re(1)–Re(2) = 3.0166(3), Re(1)–O(9) = 2.161(5), Re(2)–O(9) = 2.151(5), Re(1)–H(12) = 1.81(4) and Re(2)–H(1) = 1.81(4).

at −10.92 ppm in the ^{1}H NMR spectrum.

When a solution of **3** in acetone-d_6 solvent was then heated to 50 °C for 2 days, it was condensed into the known compound $[Re(CO)_3(\mu_3\text{-}OH]_4$ in 67% isolated yield by the loss of one CO ligand for each $Re(CO)_4$ group. $[Re(CO)_3(\mu_3\text{-}OH]_4$ has been obtained previously from the reaction of $Re_2(CO)_{10}$ with H_2O in the presence of UV irradiation [12]. Brown speculated on the possible existence of the compound **3** in a mechanism proposed for the formation of $[Re(CO)_3(\mu_3\text{-}OH]_4$, but was not able to obtain any independent evidence for its existence under their reaction conditions [12a].

3. Summary and conclusions

Upon elimination of hexene, the $Re(CO)_4$ groups in $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n]$ are each able to pass one electron to the highly unsaturated heterocumulene, *N*,*N*′-diisopropylcarbodiimide, to reduce it. Two of these reduced carbodiimide molecules are then coupled by formation of a carbon − carbon bond to yield the

diamidinate complex **2**. The mechanism for this coupling process has not been established. Models for the π-bonding in the diamidinate ligand in **2** have been developed which explain the structure of the ligand. The elusive hydroxy-hydride complex **3** was obtained in a side reaction of **1** with H_2O. Compound **3** was readily transformed to the known compound $[Re(CO)_3(\mu_3\text{-}OH]_4$ [12] by mild heating.

4. Experimental details

4.1. General data

All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet IS10 Midinfrared FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe by using electron impact ionization (EI) were made on a VG 70S instrument. $Re_2(CO)_{10}$ and *N,N′*-diisopropylcarbodiimide, i-PrNCN-i-Pr, were obtained from Pressure Chemical and Sigma Aldrich, respectively, and were used without further purification. $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$ [6] and $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** [7] were prepared according to previously reported procedures. Product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F_{254} glass plates or by chromatography over Biobeads purchased from Bio-Rad.

4.2. Reaction of $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$ with N,N′-Diisopropylcarbodiimide

A 100.0 mg amount (0.147 mmol) of $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$ and 43 μL (0.294 mmol) of *N,N′*-Diisopropylcarbodiimide were dissolved in heptane. The solution was then heated to reflux for 25 min. The solution was cooled, and the solvent was then removed in *vacuo*. The residue was extracted in hexane and filtered through a column of Biobeads by using CH_2Cl_2 solvent to give a yellow band of $[Re(CO)_4]_2[(\mu\text{-}C_2(N\{iPr\})_4]$, **2**, 68.0 mg (59% yield). Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2095(m), 1995(vs), 1971(s), 1930(s). ^{1}H NMR (CD_2Cl_2, δ in ppm): δ 3.63 (sept, $CH(CH_3)_2$, $^3J = 6.3$ Hz), 1.10 (d, CH_3, $^3J = 6.3$ Hz). Mass Spec. EI/MS *m/z*: 848, M^+, 820, M^+-CO, 792, M^+-2CO. This isotope distribution pattern is consistent with the presence of four rhenium atoms.

4.3. Reaction of 1 with N,N′-Diisopropylcarbodiimide

A 20.0 mg (0.029 mmol) amount of **1** and 4.5 μL (0.029 mmol) of *N,N′*-diisopropylcarbodiimide were dissolved in 1.6 mL CD_2Cl_2 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 40 °C for 24 h. A ^{1}H NMR spectrum obtained after this period showed the resonances of compound **2** and a hydrido resonance at $\delta = -10.92$. The contents were then transferred to a vial and solvent was removed in *vacuo*. The residue was extracted in CH_2Cl_2 and separated by TLC by using hexane/methylene chloride (50/50) solvent mixture to give a major colorless band of 5.0 mg of $Re_2(CO)_8(\mu\text{-}OH)(\mu\text{-}H)$, **3**, 28% yield. Compound **2** was not obtained in this workup by TLC on silica gel due to its decomposition on the TLC plate. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2097(m), 2016(vs), 1992(sh), 1953(s). ^{1}H NMR (CD_2Cl_2, δ in ppm): −0.30 (s, 1H, OH), −10.92 (s, 1H, hydrides). Mass Spec. EI/MS *m/z*: 614, M^+, 586, M^+-CO. The isotope distribution is consistent with the presence of two rhenium atoms. The formation of **3** in this reaction is attributed to a competing reaction of **1** with adventitious quantities of H_2O present in the carbodiimide sample.

4.4. Synthesis of 3 from reaction of 1 with H_2O

A 20.0 mg (0.029 mmol) amount of **1** and 5.0 μL (0.28 mmol) of H_2O were dissolved in 1.6 mL CD_2Cl_2 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 40 °C for 24 h. A ^{1}H NMR spectrum obtained after this period showed formation of compound **3**. The contents were then transferred to a vial and solvent was removed in *vacuo*. The residue was extracted in CH_2Cl_2 and separated by TLC by using

Table 1
Crystal data, and results for the crystallographic analyses of compounds **2** and **3**.

Compound	2	3
Empirical formula	$Re_2O_8N_4C_{22}H_{28}$	$Re_2O_9C_8H_2$
Formula weight	848.88	614.49
Crystal system	Monoclinic	Monoclinic
Lattice parameters		
a (Å)	14.2282(7)	8.7252(3)
b (Å)	10.9524(6)	15.3690(6)
c (Å)	19.078(1)	9.6605(4)
α (deg)	90.00	90.00
β (deg)	98.011(1)	93.986(1)
γ (deg)	90.00	90.00
V (Å^3)	2944.0(3)	1292.32(9)
Space group	$P2_1/c$	$P2_1/n$
Z	4	4
ρ_{calc} (g/cμ^3)	1.915	3.158
μ (Mo Kα) (mm^{-1})	8.262	18.753
Temperature (K)	294(2)	294(2)
$2\theta_{max}$(°)	56.44	56.54
No. Obs. ($I > 2\sigma(I)$)	7345	2287
No. Parameters	333	177
Goodness of fit (GOF)	1.040	1.123
Max. shift/error on final cycle	0.001	0.000
Residuals*: R1; w*R*2	0.0370; 0.0751	0.0261; 0.0655
Absorption Corr.,Max/min	Multi-Scan 1.000/0.493	Multi-Scan 1.000/0.298
Largest peak in Final Diff. Map (e$^-$/Å^3)	1.319	1.351

*$R1 = \Sigma_{hkl}(||F_{obs}|-|F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $wR2 = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2}$.
$w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

hexane/methylene chloride (50/50) solvent mixture to give a major yellow band of 11.0 mg of $Re_2(CO)_8(\mu\text{-}OH)(\mu\text{-}H)$, **3**, 60% yield.

4.5. Thermal conversion of 3 to $[Re(CO)_3(\mu_3\text{-}OH]_4$

A 10.0 mg (0.016 mmol) amount of **3** was dissolved in 1.6 mL acetone-d_6 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 50 °C for 2 days. A ^{1}H NMR spectrum obtained after this period showed formation of known compound $[Re(CO)_3(\mu_3\text{-}OH]_4$ [12]. The contents were then transferred to a vial and solvent was removed in *vacuo*. The residue was extracted with CH_2Cl_2 and separated by TLC by using hexane/methylene chloride (50/50) solvent mixture to give a colorless band of 6.0 mg of $[Re(CO)_3(\mu_3\text{-}OH]_4$ in 67% yield, confirmed by IR and ^{1}H NMR analyses [12].

4.6. Crystallographic analyses

Single crystals of compounds **2** and **3** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from solutions of the pure compounds in hexane solvent at room temperature. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT + program by using a narrow-frame integration algorithm [13]. Corrections for Lorentz and polarization effects were also applied with SAINT+. Empirical absorption corrections based on the multiple measurements of equivalent reflections were applied in each analysis by using the program SADABS [13]. All structures were solved by a combination of direct methods and difference Fourier syntheses, and were refined by full-matrix least squares refinement on F^2 by using the SHELXTL software package [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in geometrically idealized positions and were included as standard riding atoms during the final least-squares refinements. Crystal data, data collection parameters, and results for the analyses are listed in Table 1.

4.7. Computational analyses

All calculations were performed with the Amsterdam Density Functional (ADF) program library by using the PBEsol D3 functional. For additional information see the electronic Supporting Information.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.06.027.

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