Reductive coupling of diisopropylcarbodiimide by a dirhenium carbonyl complex

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ABSTRACT

The reaction of Re₂(CO)₈[µ-µ-H][µ-η²-C(H)C(H)Bu] with N,N′-diisopropylcarbodiimide yielded the new rhenium diamidinate complex [Re₂(CO)₄][µ-µ-C₂(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 modes [1]. The formation of oxalates by the C—C coupling of two equivalents of CO₂ could become an important route for recycling this major greenhouse gas and the reduction of oxalates could lead to useful C₂-organic compounds [2]. Tetrasubstituted C₂-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 aromes E are coordinated to the metal atoms (Scheme 1).

In recent studies, we have been investigating the reactivity of dirhenium complexes Re₂(CO)₈[µ-µ-H][µ-η²-C(H)C(H)C₆H₅] with aryl-gold compounds [7], with traces of N,N′-diisopropylcarbodiimide and Re₂(CO)₈[µ-µ-C₆H₅H₅][µ-H], 1. Compound 3 was subsequently found to be a product of the reaction of 1 with traces of H₂O in the original reaction and was independently obtained in 60% yield from the reaction of 1 with H₂O. 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.

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1. Introduction

The metal-assisted reductive coupling of heteroallenes by C—C bond formation can lead to a variety of tetrasubstituted C₂-products ranging from oxalate from CO₂ [1] to diamidates [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 CO₂ could become an important route for recycling this major greenhouse gas and the reduction of oxalates could lead to useful C₂-organic compounds [5].

Tetrasubstituted C₂-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 Re₂(CO)₈[µ-µ-H][µ-η²-C(H)C₆H₅] 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 Re₂(CO)₈[µ-µ-H][µ-η²-C(H)C₆H₅] with N,N′-diisopropylcarbodiimide and water. The results of these studies are reported herein.

2. Results and discussion

Re₂(CO)₈[µ-µ-H][µ-η²-C(H)C₆H₅] with N,N′-diisopropylcarbodiimide in a solution in heptane heated to reflux for 25 min provided the new compound [Re₂(CO)₄][µ-µ-C₂(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 C₂N₄ group at the C₁—C₂ bond which gives the molecule and overall D₂₅ symmetry. The dihedral angle between the two planes C₂—C₁—N₄—N₁ and 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
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 sp²-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 C2N4 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, albeit 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 Re2(CO)8(μ-OH)(μ-H), 3 which was subsequently obtained in a much better yield through an independent reaction of 1 with H2O itself, see below.

The reaction of 1 with N,N'-diisopropylcarbodiimide in the presence of small amounts of water provided the new compound Re2(CO)8(μ-OH)(μ-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 H2O 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 Re2(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 dpmp dirhenium carbonyl complex Re2(CO)8(dpmp)(μ-OH)(μ-H), dpmp = 12-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
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 $\text{[Re(CO)₃(μ₃-OH)]₄}$ in 67% isolated yield by the loss of one CO ligand for each Re(CO)$_4$ group. $\text{[Re(CO)₃(μ₃-OH)]₄}$ has been obtained previously from the reaction of Re$_2$(CO)$_{10}$ with H$_2$O 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 $\text{[Re(CO)₃(μ₃-OH)]₄}$, 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)$_{10}$(μ-H)[μ-η$^2$-C(H)═C(H)Bu]$^+$ are each able to pass one electron to the highly unsaturated heterocumulene, N,N′-disopropylcarbodiimide, to reduce it. Two of these reduced carbodiimide molecules are then coupled by formation of a carbon — carbon bond to yield the
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. 1H 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 operating at 300 MHz. Mass spectrometric (MS) measurements were performed by a direct-exposure probe by using electron impact ionization (EI) were made on a VG 70S instrument. Re2(CO)8 and N,N'-diisopropylcarbodiimide, i-PrNCN-i-Pr, were obtained from Pressure Chemical and Sigma Aldrich, respectively, and were used as received. The elusive hydroxy-hydride complex 3 was readily transformed to the known compound [Re(CO)3(CH3-OH)]4 [12] by mild heating.

4.2. Reaction of Re2(CO)8 with N,N'-diisopropylcarbodiimide

A 100.0 mg (0.147 mmol) amount of Re2(CO)8 was dissolved in 1.6 mL CD2Cl2 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 1H NMR spectrum obtained after this period showed the resonances of compound 2 and a hydrido resonance at δ = –10.92. The contents were then transferred to a vial and solvent was removed in vacuo. The residue was extracted in CH3Cl2 and separated by TLC using hexane/methylene chloride (50/50) solvent mixture to give a major colorless band of 5.0 mg of Re2(CO)8 and a hydrido band of 4.5 mg of Re2(CO)8(μ-OH)(μ-H), 28% yield. Compound 2 was not obtained in this workup by TLC on silica gel plates or by chromatography over Biobeads purchased from Bio-Rad.

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 CD2Cl2 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 1H NMR spectrum obtained after this period showed the resonances of compound 2 and a hydrido resonance at δ = –10.92. The contents were then transferred to a vial and solvent was removed in vacuo. The residue was extracted in CH3Cl2 and separated by TLC using hexane/methylene chloride (50/50) solvent mixture to give a major colorless band of 5.0 mg of Re2(CO)8(μ-OH)(μ-H), 28% yield. Compound 2 was not obtained in this workup by TLC on silica gel plates or by chromatography over Biobeads purchased from Bio-Rad.

4.4. Synthesis of 3 from reaction of 1 with H2O

A 20.0 mg (0.029 mmol) amount of 1 and 5.0 μL (0.28 mmol) of H2O were dissolved in 1.6 mL CD2Cl2 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 1H 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 CH3Cl2 and separated by TLC using hexane/methylene chloride (50/50) solvent mixture to give a major colorless band of 4.5 mg of Re2(CO)8(μ-OH)(μ-H), 28% yield. Compound 2 was not obtained in this workup by TLC on silica gel plates or by chromatography over Biobeads purchased from Bio-Rad.

Table 1

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Largest peak in Final Diff. Map (e/Å³)
hexane/methylene chloride (50/50) solvent mixture to give a major yellow band of 11.0 mg of \( \text{Re}_2(\text{CO})_8(\text{C}_2\text{O}_4)^{-2} \) and 11.0 mg of \( \text{Re}_2(\text{CO})_8(\text{C}_2\text{O}_4)^{-2} \) and the reductive coupling of \( \text{CO}_2 \) to oxalic acid. Inorg. Chem. 37 (1998) 4741.

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.

Acknowledgements

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Appendix A. Supplementary data

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

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