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Formation of *N,N*-Dimethylacrylamide by a Multicenter Hydrocarbamoylation of C_2H_2 with *N,N*-Dimethylformamide Activated by $Ru_5(\mu_5\text{-}C)(CO)_{15}$

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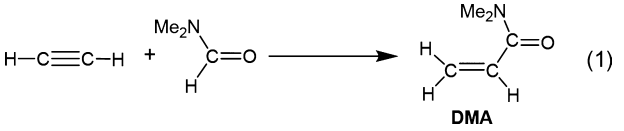
Supporting Information

ABSTRACT: Hydrocarbamoylation of C_2H_2 by *N,N*-dimethylformamide (DMF) to *N,N*-dimethylacrylamide was effected by a series of cluster-opening reactions with $Ru_5(\mu_5\text{-}C)(CO)_{15}$ (**1**). The reaction of **1** with DMF yielded the new complexes $Ru_5(\mu_5\text{-}C)(CO)_{14}(\mu\text{-}\eta^2\text{-}O{=}CNMe_2)(\mu\text{-}H)$ (**2**) and a minor coproduct $Ru_5(\mu_5\text{-}C)(CO)_{13}(HNMe_2)(\mu\text{-}\eta^2\text{-}O{=}CNMe_2)(\mu\text{-}H)$ (**3**) by a cluster-opening activation of the formyl C−H bond of DMF. Compound **3** was obtained from **2** by a further reaction with DMF. Compound **3** reacted with C_2H_2 (1 atm, 70 °C) to yield $Ru_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-}\eta^3\text{-}O{=}CNMe_2CHCH)(\mu\text{-}H)$ (**4**) by the addition and coupling of C_2H_2 to the bridging dimethylformamido ligand. Compound **4** contains a σ−π-coordinated, dimethylformamido-substituted vinyl ligand that bridges a Ru−Ru edge of an open Ru_5C cluster. The formamido group is also coordinated to one of the metal atoms. The addition of CO (1 atm, 25 °C) to **4** yielded the CO adduct $Ru_5(\mu_5\text{-}C)(CO)_{14}(\eta^2\text{-}O{=}CNMe_2CH{=}CH)(\mu\text{-}H)$ (**5**) containing a chelating dimethylacrylamido ligand, which released dimethylacrylamide by the reductive elimination of a C−H bond upon a further addition of CO (400 psi, 125 °C) with the re-formation of **1**. All of the products were characterized by single-crystal X-ray diffraction analyses.

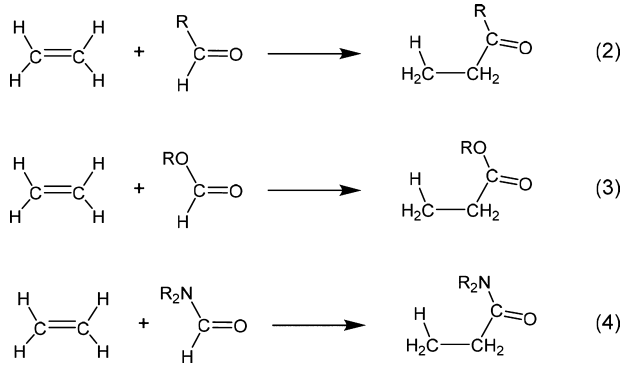
Acrylamides, like other acryloyl compounds, are precursors to a range of valuable polymers.[1] As a result, the syntheses of these acryloyl compounds have received considerable attention.[2] We have now found that *N,N*-dimethylacrylamide (DMA) can be obtained by the hydrocarbamoylation of C_2H_2



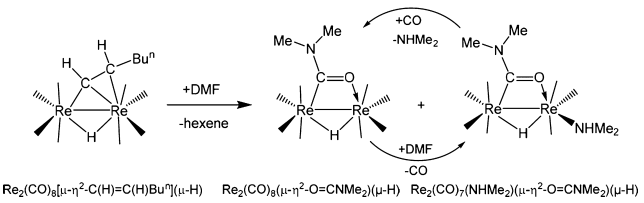
(1)

by *N,N*-dimethylformamide (DMF; eq 1) in a series of reactions facilitated by a combination of the activation of the formyl C−H bond of DMF and the addition of C_2H_2 to the cluster complex $Ru_5(\mu_5\text{-}C)(CO)_{15}$ (**1**).

While the activation and functionalization of C−H bonds by metal atoms have received much attention in recent years, most studies have been focused on the activation of aliphatic[3] and aromatic[4] C−H bonds. Hydroacylations[5] (eq 2), hydroesterifications[6] (eq 3), and even hydrocarbamoylations[7] (eq 4) of olefins and alkynes by metal complexes have been effected by the activation of formyl C−H bonds, but mechanistic details are rarely provided.



Scheme 1. Reaction and Interconversions of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ with DMF



In recent studies, we have found that the dinuclear rhenium complex $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ reacts with DMF by the elimination of 1-hexene and activation of the formyl C−H bond to yield the complexes $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}O{=}CNMe_2)(\mu\text{-}H)$ and $Re_2(CO)_7(NHMe_2)(\mu\text{-}\eta^2\text{-}O{=}CNMe_2)(\mu\text{-}H)$, both of which contain a bridging *N,N*-dimethylformamido ligand (see Scheme 1).[8]

We have now found that the pentaruthenium carbonyl complex[9] **1** reacts with DMF by activation of the formyl C−H bond to yield the new dimethylformamido complex $Ru_5(\mu_5\text{-}C)(CO)_{14}(\mu\text{-}\eta^2\text{-}O{=}CNMe_2)(\mu\text{-}H)$ (**2**; 64% yield) together with a minor, but important coproduct $Ru_5(\mu_5\text{-}C)(CO)_{13}(HNMe_2)(\mu\text{-}\eta^2\text{-}O{=}CNMe_2)(\mu\text{-}H)$ (**3**; 3% yield). Compounds **2** and **3** were also obtained independently, albeit in low yields 12% and 14%, respectively, from the reaction of **1** with $NHMe_2$. Compound **3** was also obtained from **2** (71%

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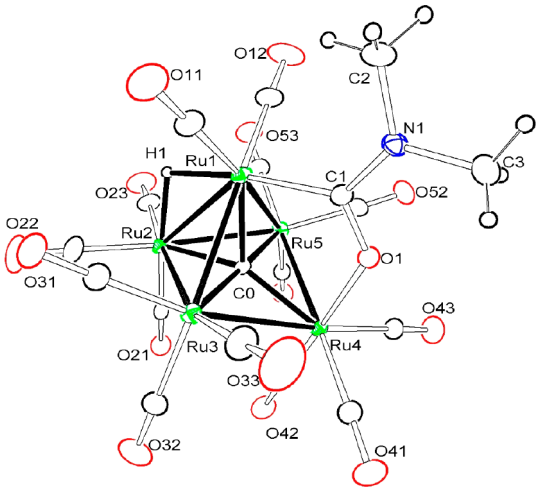

Figure 1. ORTEP diagram of the molecular structure of **2** showing 15% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru3 = 2.8349(6), Ru1−Ru5 = 2.8265(5), Ru1−Ru2 = 2.8890(5), Ru2−Ru5 = 2.8588(5), Ru2−Ru3 = 2.8606(6), Ru3−Ru4 = 2.8690(5), Ru4−Ru5 = 2.8760(5), Ru1−H1 = 1.79(5), Ru2−H1 = 1.80(5), Ru1−C1 = 2.067(4), Ru4−O1 = 2.100(3), C1−O1 = 1.280(5).

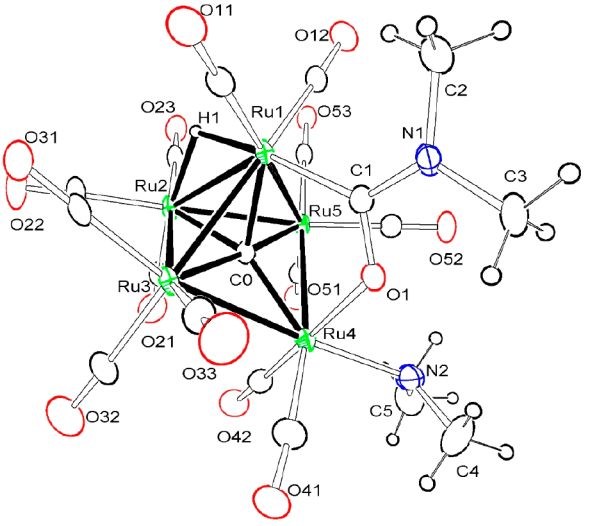

Figure 2. ORTEP diagram of the molecular structure of **3** showing 20% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru3 = 2.8087(11), Ru1−Ru5 = 2.8184(11), Ru1−Ru2 = 2.8950(11), Ru2−Ru5 = 2.8544(11), Ru2−Ru3 = 2.8541(12), Ru3−Ru4 = 2.8776(12), Ru4−Ru5 = 2.9049(12), Ru1−H1 = 1.77(8), Ru2−H1 = 1.82(8), Ru4−N2 = 2.201(11), Ru1−C1 = 2.072(10), Ru4−O1 = 2.090(7), C1−O1 = 1.299(12).

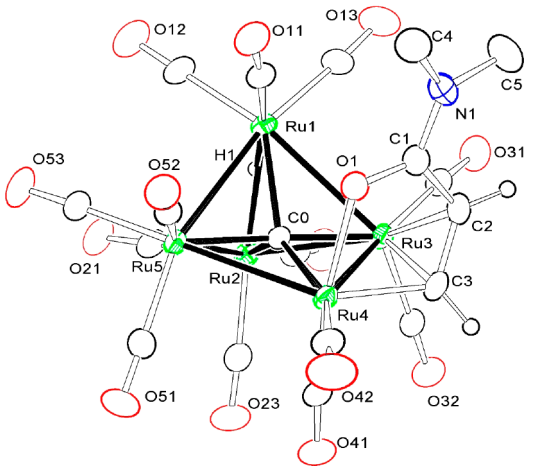

Figure 3. ORTEP diagram of the molecular structure of **4** showing 25% thermal ellipsoid probability. The methyl hydrogen atoms have been omitted for clarity. Selected interatomic bond distances (Å) are as follows: Ru1−Ru3 = 2.9491(5), Ru1−Ru5 = 2.8531(5), Ru1−Ru2 = 2.8248(5), Ru2−Ru5 = 2.8986(5), Ru2−Ru3 = 2.8409(5), Ru3−Ru4 = 2.7279(5), Ru4−Ru5 = 3.0092(5), Ru1−H1 = 1.70(6), Ru2−H1 = 1.60(6), Ru4−C3 = 2.013(4), Ru4−O1 = 2.114(2), Ru3−C2 = 2.262(4), Ru3−C3 = 2.186(4), C1−O1 = 1.264(5).

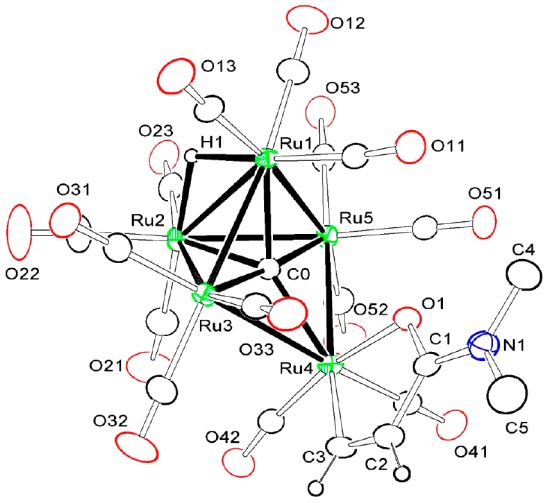

Figure 4. ORTEP diagram of the molecular structure of **5** showing 20% thermal ellipsoid probability. Methyl hydrogen atoms have been omitted for clarity. Selected interatomic bond distances (Å) are as follows: Ru1−Ru3 = 2.8437(5), Ru1−Ru5 = 2.8301(5), Ru1−Ru2 = 2.8458(5), Ru2−Ru5 = 2.8471(5) Ru2−Ru3 = 2.8706(5), Ru3−Ru4 = 2.9501(5), Ru4−Ru5 = 2.9549(5), Ru1−H1 = 1.66(4), Ru2−H1 = 1.79(4), Ru4−C3 = 2.034(5), Ru4−O1 = 2.155(3), C1−O1 = 1.282(5), C1−C2 = 1.452(7), C2−C3 = 1.330(8).

yield) by the reaction with an additional quantity of DMF at 98 °C for 8 h and by a direct reaction of **2** with $NHMe_2$. The $NHMe_2$ ligand was presumably formed by decarbonylation of DMF in the first reaction. Other metal complexes have been shown to decarbonylate DMF via pathways that involve an initial activation of the formyl C−H bond.[10] Both compounds were characterized by IR, ^{1}H NMR, mass spectrometry, and single-crystal X-ray diffraction analyses. ORTEP diagrams of the molecular structures of **2** and **3** are shown in Figures 1 and 2, respectively. Both compounds contain a hydrido ligand that bridges the Ru1−Ru2 bond, δ −21.47 and δ −21.99, in the ^{1}H NMR spectra of **2** and **3**, respectively, and a bridging dimethylformamido ligand formed by cleavage of the formyl C−H bond of DMF and its addition to the Ru_3 cluster. One Ru−Ru bond in the cluster was cleaved by the addition and the μ-η^2-O=C-dimethylformamido ligand that bridges the opened edge of the Ru_3 cluster. In combination, the bridging formamido and hydrido ligands in **2** formally donate four electrons to the metal atoms, but **1** loses only one CO ligand (two electrons) in the formation of **2**. Thus, the opening of the cluster by the cleavage of one of the Ru−Ru bonds plays a key role in the success of the reaction by providing the equivalent of another "vacant" coordination site for the two additional electrons. In addition, the carbido carbon atom C0 plays an

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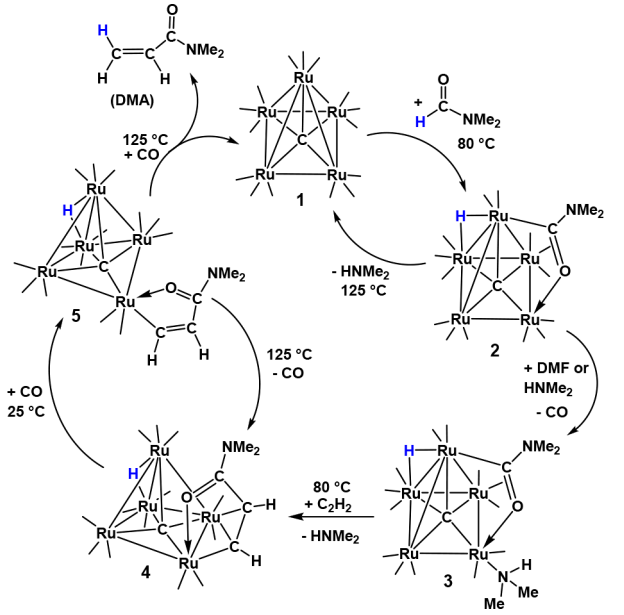
Scheme 2. Schematic of the Hydrocarbamoylation of C_2H_2 with DMF by 1



important role by holding the cluster together. Compound **3** contains an $NHMe_2$ ligand on one of the metal atoms, Ru4, in place of one of the terminal CO ligands in **2** [Ru4−N2 = 2.201(11) Å].

Most interestingly, complex **3** was found to react with C_2H_2 under a slow purge (1 atm) at 70 °C for 5 h to yield the new complex $Ru_5(\mu_5\text{-C})(CO)_{13}[\mu\text{-}\eta^3\text{-O}{=}CN(Me)_2CHCH](\mu\text{-H})$ (**4**; 6% yield). Compound **4** was characterized crystallographically, and an ORTEP diagram if its molecular structure is shown in Figure 3. Compound **4** contains a dimethylformamido-substituted, σ−π-vinyl ligand that bridges the Ru3−Ru4 edge of the open Ru_5C cluster by the carbon atoms C2 and C3 [Ru3−C2 = 2.262(4) Å, Ru3−C3 = 2.186(4) Å, and Ru4−C3 = 2.013(4) Å]. The formamido group is coordinated to Ru4 by its oxygen atom O1 [Ru4−O1 = 2.114(2) Å]. This unusual ligand was formed from displacement of the labile $NHMe_2$ ligand from **3** followed by the addition and C−C coupling of C_2H_2 to the carbon end of the bridging formamido ligand. Interestingly, we have not been able to obtain **4** from **2** by reaction with C_2H_2. Presumably, this is because C_2H_2 is not able to displace the more strongly coordinated CO ligands on **2**.

When treated with CO at 1 atm and 25 °C, a CO adduct of **4**, $Ru_5(\mu_5\text{-C})(CO)_{14}[\eta^2\text{-O}{=}CN(Me)_2CH{=}CH](\mu\text{-H})$ (**5**), was formed in 38% yield. An ORTEP diagram of the molecular structure of **5** is shown in Figure 4.

Compound **5** contains a chelating η^2-dimethylformamido-substituted vinyl ligand coordinated to Ru4 by the amido oxygen atom O1 [Ru4−O1 = 2.155(3) Å] and the terminal olefin carbon atom C3 [Ru4−C3 = 2.034(5) Å and C2−C3 = 1.330(8) Å]. Compound **5** was converted back to **4** (52% yield) by thermal decarbonylation (125 °C, 1 h) with complete restoration of π coordination of C=C.

Most interestingly, when treated with CO under more forcing conditions (400 psi, 125 °C for 3 h), DMA was released from **5** (confirmed by ^{1}H NMR spectral analysis) and compound **1** was formed in 71% yield.

The sequence of transformations is overall tantamount to the hydrocarbamoylation of C_2H_2 by DMF (eq 1). Although regeneration of **1** in the final step formally closes what could be considered to be a "catalytic" cycle (Scheme 2), the reaction is not yet effectively catalytic because of certain low yield transformations, such as **3** to **4**, and the use of CO, which effectively inhibits the second loop through the cycle that requires additional reactions with DMF.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00460.

Synthetic details and NMR spectroscopic data along with structural characterizations of the new compounds (PDF)

Accession Codes

CCDC 1824915−1824918 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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