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Reaction Mechanisms

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Direct Evidence for the Attack of a Free N-Heterocyclic Carbene at a Carbonyl Ligand: A Zwitterionic Osmium Carbonyl Cluster**

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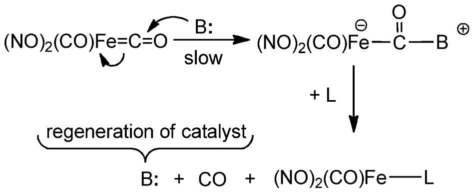
Interest in the organometallic chemistry of N-heterocyclic carbenes (NHCs) and their mesoionic analogues (mNHCs) remains as high as ever,[1] and this interest has naturally been carried over into organometallic cluster chemistry.[2] The chemistry of NHCs with transition-metal carbonyl clusters was reviewed recently.[3] The first Group 8 trinuclear carbonyl cluster containing an NHC ligand, $[Ru_3(CO)_{11}(sIEt)]$ (sIEt = *N,N'*-diethylimidazolidin-2-ylidene), was reported in 1977.[4] The pace picked up, however, only almost 30 years later when Cabeza et al. reported that the reactivity of NHCs with $[M_3(CO)_{12}]$ (M = Ru, Os) depended strongly on the nature of the substituent on the NHC: the more basic and less bulky the NHC ligand, the more facile its reaction with the metal clusters. It was found that $[Ru_3(CO)_{12}]$ reacted readily with *N,N'*-dimethylimidazolin-2-ylidene (IMe) at room temperature to give the trinuclear derivative $[Ru_3(CO)_{11}(IMe)]$. With the bulkier NHC *N,N'*-dimesitylimidazolin-2-ylidene (IMes), the reaction afforded the trinuclear analogue and the hexanuclear salt $[IMes{\cdot}H][Ru_6(\mu_3\text{-}CO)_2(\mu\text{-}CO)_2(CO)_{14}]$, and with *N,N'*-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr), only the analogous hexanuclear salt was obtained.[5] A 1:3 reaction stoichiometry with IMes or IPr generated the mononuclear $[Ru(CO)_4(NHC)]$ instead.[6] The analogous reaction of IMe with $[Os_3(CO)_{12}]$ gave $[Os_3(CO)_{11}(IMe)]$, but the bulkier carbene IMes and IPr failed to react even at temperatures as high as 70 °C.[7] Interestingly, it was reported that *N,N'*-di-*tert*-butylimidazolin-2-ylidene (I*t*Bu) reacted with $[Ru_3(CO)_{12}]$ at room temperature to give the mesoionic (abnormal) NHC complex $[Ru_3(CO)_{11}(\text{mI}t\text{Bu})]$ in which the NHC was coordinated through the C4 atom.[8] The even bulkier NHC *N,N'*-bis(adamantyl)imidazolin-2-ylidene (IAd) also reacted with both $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ at 70 °C to generate the mesoionic NHC complexes $[M_3(CO)_{11}(\text{mIAd})]$.[9]

All these reactions can be described as overall carbonyl-substitution reactions, in which a carbonyl ligand has been substituted by an NHC, either in the normal or in the mesoionic coordination mode. Several pathways for the substitution of carbonyl ligands have been proposed over the years. Of particular relevance in these reactions is that which involves nucleophilic attack at the carbonyl carbon atom. Such a mechanism has been demonstrated in several different chemical situations, for example, with organolithium compounds,[10] Grignard reagents,[11] methoxide,[12] and hydroxide,[13] in reactions of $[FeCp(CO)_2L]$ with nucleophiles, such as primary and secondary amines and alkoxides,[14] and in the activation of cyclopentadienyl ruthenium complexes by *t*BuOK in the racemization of alcohols.[15]

In many cases, the base interacts with the carbon atom of the carbonyl ligand to form a weak acid–base adduct. For example, in a study of different base-catalyzed substitution reactions of $[Fe(CO)_2(NO)_2]$, Morris and Basolo proposed that the base catalysts functioned by attacking the carbonyl carbon atom (hard) and not the metal (soft) (Scheme 1).[16]



Scheme 1. Base-catalyzed pathway in $[Fe(CO)_2(NO)_2]$.

Kaesz and co-workers also suggested that anionic nucleophiles attacked the complexes $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ at the carbon atom of a CO ligand to form η^1-C(O)Nu-substituted trinuclear anions (in which Nu is the nucleophile).[17] To the best of our knowledge, however, no intermediate has ever been isolated from these reactions.

Herein, we report the results of our investigations into the reaction of free NHCs with $[Os_3(CO)_{12}]$. In contrast to earlier studies, which were carried out with NHCs generated in situ, we found that the reaction of the complex upon direct treatment with a free NHC appears to proceed through initial attack of the NHC at a carbonyl carbon atom. The intermediate acyl complex thus formed turned out to be sufficiently stable to be isolated and characterized crystallographically.

The reaction of the free N-heterocyclic carbene IMes (**1a**; 1.5 equiv) with $[Os_3(CO)_{12}]$ (**2**) in THF at room temperature afforded $[Os_3(CO)_{11}\{C(=O)m\text{IMes}\}]$ (**3a**) as the major product (39 % yield) together with $[Os_3(CO)_{11}(m\text{IMes})]$ (**4a**),

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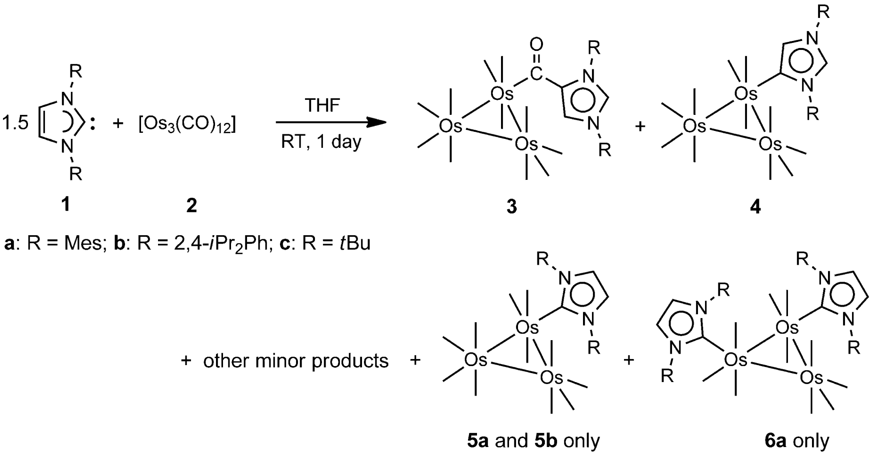


Scheme 2. Reaction of free NHCs **1** with the triosmium cluster **2**.

$[Os_3(CO)_{11}(IMes)]$ (**5a**), $[Os_3(CO)_{10}(IMes)_2]$ (**6a**), and small amounts of other products (Scheme 2). The analogous products $[Os_3(CO)_{11}\{C(=O)m\mathrm{IPr}\}]$ (**3b**) and $[Os_3(CO)_{11}\{C(=O)m\mathrm{I}t\mathrm{Bu}\}]$ (**3c**) were obtained similarly from IPr (**1b**) and ItBu (**1c**). Clusters **3a–c**, **4a**, and **6a** were all structurally characterized. Of particular interest are the structures of the clusters **3**; the ORTEP plot showing the molecular structure with selected bond parameters for **3a** is given in Figure 1. For comparison, the structure of **4a** is shown in Figure 2.

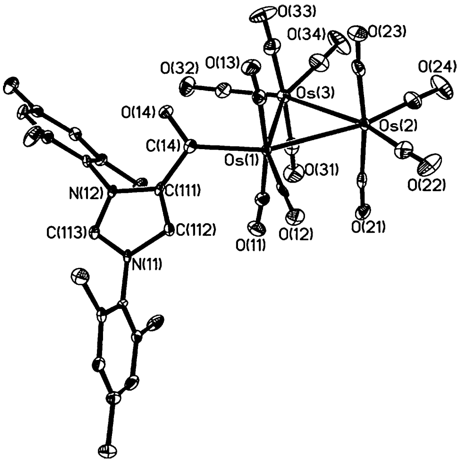


Figure 1. ORTEP plot for $[Os_3(CO)_{11}(C(=O)m\mathrm{IMes})]$ (**3a**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms on the organic moieties are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os(1)–Os(2) 2.8795(4), Os(1)–Os(3) 2.8795(4), Os(2)–Os(3) 2.9033(4), Os(1)–C(14) 2.081(7), C(14)–O(14) 1.226(8), C(14)–C(111) 1.509(9); O(14)-C(14)-Os(1) 126.3(5), C(111)-C(14)-Os(1) 120.1(4), O(14)-C(14)-C(111) 113.6(6).

Cluster **3a** is stable to air in the solid state for a few days. It is insoluble in hexane and completely soluble in THF, acetone, and dichloromethane, although it decomposed slowly in solution at room temperature to give **2** (by loss of the NHC ligand), **4a** (by loss of a CO ligand), and other unknown species. However, **4a** is relatively stable and did not decompose in THF even when CO gas was bubbled into the solution for several hours. Consistent with the structure of the complexes, the IR spectrum of **3a** is similar to that for **4a**, except for the presence of two very weak peaks at 1577 and 1531 cm^{-1}. These absorptions were assigned to the acyl group, although a computational study suggested that they are not pure C=O stretches, but are coupled to ring deformations of the imidazole (see below).

The $^{13}C\{^1H\}$ NMR spectrum of **3a** in [D$_8$]THF at −30 °C was assigned on the basis of ^1H-$^{13}C\{^1H\}$ HMQC/HMBC and DEPT-90 experiments. Resonances were observed at $\delta = 139.0$ and 129.3 ppm for the two C–H carbon atoms of the imidazole ring, at $\delta = 148.4$ ppm for the ring carbon atom attached to the acyl group, and at $\delta = 203.9$ ppm for the acyl group. As may be expected, a particularly large downfield shift was observed for the resonance due to the ring carbon atom attached to the acyl group as compared to the corresponding resonances in **4a** and **5a** ($\delta = 122.9$ and 123.7 ppm, respectively). The imidazole ring also showed two doublets at $\delta = 9.00$ and 8.27 ppm in the ^1H NMR spectrum; these signals, especially the latter, are shifted significantly downfield from the corresponding resonances in **4a** ($\delta = 8.78$ and 6.83 ppm).

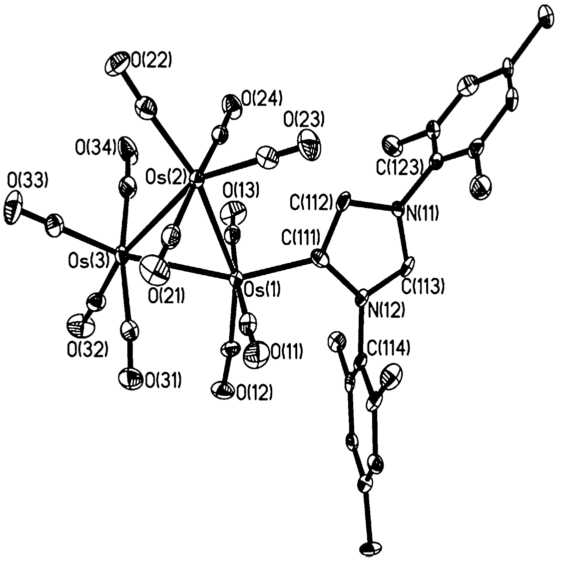


Figure 2. ORTEP plot for $[Os_3(CO)_{11}(m\mathrm{IMes})]$ (**4a**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms on the organic moieties are omitted for clarity. Selected bond lengths [Å]: Os(1)–Os(2) 2.8854(4), Os(1)–Os(3) 2.8650(5), Os(2)–Os(3) 2.8814(5), Os(1)–C(111) 2.126(8).

On the basis of electron-counting rules, the clusters **3** should be regarded as zwitterionic, with a negative charge on the cluster and a positive charge at the NHC ring. This electronic structure was examined by natural bond orbital (NBO) analysis of a simplified computational model with R =

H. The total charge computed for the imidazole ring was +0.81, whereas that for the $[Os_3(CO)_{11}]$ moiety was −0.64. We believe that the surprising stability of the zwitterionic complexes **3** can be attributed to the delocalization of these charges onto the cluster moiety and the imidazole ring, respectively.

The atom–atom overlap-weighted NAO bond orders for the Os–Os vectors are roughly equal (Figure 3; NAO = natural atomic orbital). Although NAO bond orders involving heavy transition-metal atoms are not expected to be very reliable, that for the osmium–acyl bond of 0.84, as compared to an average of approximately 1.2 for an osmium–carbonyl bond, as well as the values for the acyl C=O bond (1.19) and the acyl–imidazole bond (0.90), suggests that it should be regarded as a single bond. These values are also consistent with the bond parameters from the crystal structures of complexes **3**; for example, the values for **3a** are 1.226(8) Å for the acyl C=O, 1.509(9) Å for the acyl–imidazole, and 2.081(7) Å for the osmium–acyl vectors. The bond parameters for the imidazole rings in **3a** and **4a** are otherwise comparable.

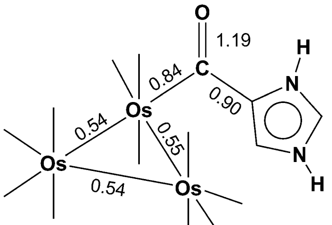
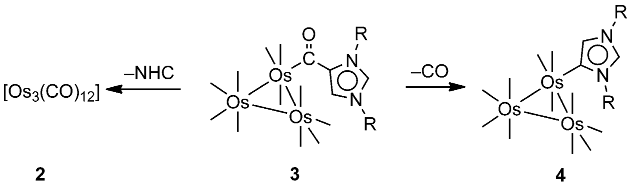


Figure 3. Atom–atom overlap-weighted NAO bond order for **3**.

We confirmed our hypothesis that **3a** was the precursor to **4a** by monitoring a solution of **3a** in THF by ^{1}H NMR spectroscopy. Ar was bubbled through the solution to remove any CO released, and it was found that **3a** was slowly converted into **4a** over a period of 4 days. TLC separation of the final reaction mixture afforded **4a** as the major product. In a Carius NMR tube, the conversion was very slow. These results suggest that the initial site of attack by the NHC is the carbon atom of a carbonyl ligand to form a zwitterionic acyl intermediate **3**. It is well-established that free NHCs can give rise to mesoionic NHC complexes.[8,9,18] Mesoionic imidazolin-4/5-ylidenes are also stronger σ donors than normal imidazolin-2-ylidenes[19] and tend to dissociate from the metal more readily.[20] A migratory deinsertion from **3** would afford **4** (Scheme 3), and **5** presumably results from a similar pathway through attack of the NHC as a normal carbene. The parent cluster **2** is known to be quite inert with respect to CO dissociation. Presumably, therefore, the migratory deinsertion step in **3** is aided by the presence of the acyl ligand, which labilizes a *cis* CO ligand towards dissociation. This reaction pathway is essentially identical to that proposed by Basolo and Morris,[16a,b] but with a small difference. According to that proposal, the attack of the base at a CO ligand forms the acyl ligand, which facilitates CO loss. The resulting vacant coordination site is then taken up by the incoming ligand. In our case, we believe that the same ligand (NHC) is involved in both the formation of the acyl group and the substitution steps. We found that the reaction of free IMes with **3a** was very rapid and afforded a complex mixture, which did not appear to contain any of **4a**–**6a** (see the Supporting Information). That the mechanism proposed by Basolo was also operative, however, would account for why cluster **3** was not reported by earlier researchers; they employed NHCs that were generated in situ, and hence the reaction mixtures would have contained other reagents, such as KO*t*Bu, *t*BuOH and KCl, which would have catalyzed the carbonyl substitution.



Scheme 3. Relationship of **2**–**4** in terms of the reaction pathway.

We also attempted to examine the reaction **3**→**4** + CO computationally on the basis of DFT. Simplified models of the complexes, in which the N substituents were replaced with H atoms, were used. The free-energy changes relative to that of **3** for the reaction pathway are given in Figure 4. The overall reaction is exergonic, with a change in the Gibbs free energy of $-144\,\mathrm{kJ\,mol^{-1}}$. The first step involves the elimination of a CO ligand to form intermediate **A**. We attempted to locate the global minimum for **A** by generating three initial geometries from the optimized structure for **3** and then removing in turn each of the CO ligands on the Os atom bearing the acyl group. The lowest-energy structure obtained in this way is shown; it corresponds a ΔG° value of $-29\,\mathrm{kJ\,mol^{-1}}$ for the loss of the CO group. The loss of an alternative CO ligand from a neighboring Os atom was also examined, but was found to be fairly endergonic

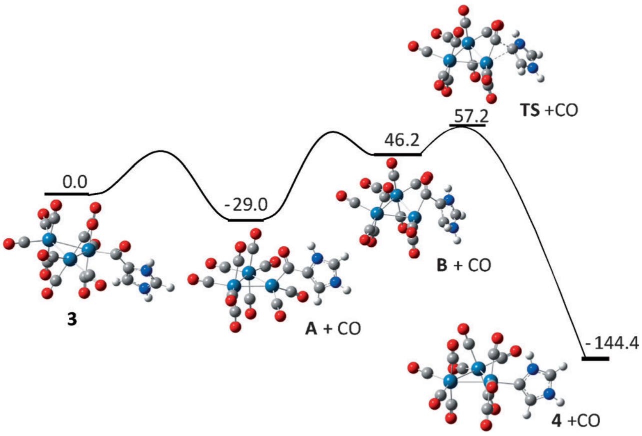


Figure 4. Computed changes in the relative free energy (in $\mathrm{kJ\,mol^{-1}}$, with respect to **3**) for the reaction **3**→**4** + CO. Simplified models of the complexes, in which the N substituents were replaced with H atoms, were used.

($+82\,\mathrm{kJ\,mol^{-1}}$). From **A**, it appears that isomerization to another intermediate **B** is likely. In **B**, the acyl ligand is rotated into an axial position and resembles the transition state **TS**, which connects **B** with **4**.

In conclusion, we have reported herein that the reaction of a free NHC with $[\mathrm{Os_3(CO)_{12}}]$ appears to proceed through initial attack of the NHC ligand on the carbon atom of a carbonyl ligand to form an acyl ligand. The product of this initial reaction is a surprisingly stable zwitterion, which was isolated and completely characterized. Although widely proposed in transition-metal carbonyl chemistry, such an intermediate had never before been structurally characterized. We also demonstrated that this intermediate subsequently loses a CO ligand, and showed computationally that a migratory deinsertion of the acyl ligand leads to overall carbonyl substitution. We believe that this reaction pathway may be applicable to many carbonyl-substitution reactions involving NHCs and, presumably, other neutral nucleophiles. Studies are currently under way to verify the generality of this mechanism.

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