Non-classical NHC transfers from the reaction of (IMes)AgCl with osmium carbonyl clusters[†]

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Received 28th February 2007, Accepted 2nd March 2007 First published as an Advance Article on the web 26th March 2007 DOI: 10.1039/b703071c

N-Heterocyclic carbene transfer reactions were attempted using IMesAgCl and two osmium clusters. The products isolated from these reactions suggest that NHC transfers can be unpredictable.

N-Heterocyclic carbenes (NHCs) are important ligands in organometallic chemistry. They provide a versatile alternative to phosphine ligands, often showing stronger electron-donating properties while also providing more variable steric environments than those observed for phosphines.¹ The reaction of free NHCs can be technically demanding owing to their highly reactive nature. NHC-silver(I) halide complexes are an attractive class of molecules with the potential for direct transmetallation of the NHC ligand. This reaction is accompanied by the thermodynamically favourable formation of solid silver(I) halide, which typically precipitates during the course of the reaction. As NHC-silver(I) halide complexes are generally air- and moisture-stable, these reagents allow for an easy starting point into the area of NHCmetal chemistry. Several research groups have investigated the use of silver(I) halide complexes as NHC transfer agents and have successfully prepared NHC complexes of several late transition metals by this method.^{2,3} A general scheme depicting the intended reactivity is outlined in eqn (1).

$$NHC-Ag-X \rightarrow NHC-ML_n \rightarrow NHC-ML_n + AgX_{(s)}$$
 (1)

We began our investigation on the reaction of NHC-silver(I) chloride as an NHC transfer agent to various osmium clusters as an entry point into this emerging field. Due to relativistic effects and lanthanide contraction, osmium compounds have the ability to adopt a variety of novel structural architectures possessing maximized orbital overlap with various ligands. Furthermore, osmium has a remarkable ability to concatenate. The diversity of metallic skeletal arrangements provides for a wide variety of ligand-stabilised osmium cluster compounds. In addition, the ability to readily remove CO from osmium carbonyl‡ clusters makes them amenable to both facile ligand substitution and to the introduction of various metal-containing species. This leads to the formation of novel mixed metal compounds. Finally, the presence of CO ligands provides a ready spectroscopic handle for monitoring reaction progress and ligand effects via IR spectroscopy. These characteristics make osmium carbonyl cluster compounds an ideal system for the study of NHC transfer reactions and synthetic transition metal chemistry.⁴ We also note that although NHCs are common ligands in transition metal complexes, Os–NHC complexes are rare, and are unknown for polynuclear osmium clusters.⁵

With these features in mind, $Os_3(\mu-H)_2(CO)_{10}$ was reacted with an equimolar amount of [(IMes)AgCl]), IMes = bis(1,3-(2,4,6trimethylphenyl)imidazol-2-ylidene) in a $2:3 \text{ CH}_2\text{Cl}_2$: hexanes mixture. The reaction vessel was degassed three times using freeze-pump-thaw techniques, and the purple reaction mixture was warmed in an oil bath overnight at 60 °C. At the end of this time, the reaction vessel contained an orange-yellow solution and a small amount of dark solid was present at the bottom of the vessel. The solvent was removed in vacuo and the remaining solid dissolved in a minimum of CH2Cl2 and applied to a silica gel column. Elution under a 30% solution of CH₂Cl₂ to hexanes afforded an orange-yellow band of 1.§ This band was eluted, the solvent removed, and the solid residue was dissolved in a hot hexanes and toluene solution to afford 1 as orange-red crystals upon concentration. Other bands were also eluted and these correspond to $Os_3(\mu-H)_2(CO)_{10}$ and $Os_3(CO)_{12}$ as determined by infrared spectroscopy. Please note that in all reactions performed in this study complex mixtures of products were obtained. These mixtures were separated and purified using column chromatography. Although often a concern, product rearrangement or decomposition on silica gel columns was not observed. In all cases crude reaction mixtures were analyzed by infrared spectroscopy as were the isolated products. The appearance of v(CO) bands appeared to be consistent in both position and relative intensity following chromatography, leading us to believe no rearrangement or decomposition of reaction products had occurred

¹H and ¹³C{¹H} NMR solution studies on the crystalline solid material **1** revealed the presence of an asymmetrically oriented **IMes** ligand. ¹H NMR studies also revealed a single resonance at -13.3 ppm that integrates to one hydrogen atom, which indicates that one of the hydride ligands had been lost from the osmium cluster. IR solution studies on a hexanes solution of **1** indicated the presence of eight ν (CO) bands. In order to determine the atom connectivity we performed a crystallographic study.¶* Single crystals were grown and the results of the study are shown in Fig. 1.

The solid state structure of **1** shows the anticipated formation of an **NHC** osmium carbonyl cluster complex, but not the one predicted by eqn (1). The molecule can be viewed as an **NHC** complex of the osmium carbonyl cluster $Os_3(\mu-H)(\mu-Cl)(CO)_9$, where an **NHC** occupies a coordination site previously engaged by a CO ligand in $Os_3(\mu-H)_2(CO)_{10}$, and a hydride ligand has been replaced by a chloride ligand. By mass balance, the reactants $Os_3(\mu-H)_2(CO)_{10}$ and [(**IMes**)AgCl] are incorporated into the final

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product with concomitant loss of "AgH", which presumably disproportionates to elemental silver and H_2 .

Another new type of reactivity was observed upon reaction of equimolar amounts of [(**IMes**)AgCl] with another activated osmium species, $[Os_3(CO)_{10}(CH_3CN)_2]$. The reaction progress was followed by IR spectroscopy over 2 h at room temperature by monitoring the disappearance of bands in the CO stretching region, specifically 2023 cm⁻¹. During the reaction, no observable precipitate of AgCl was formed, in contrast to standard transfer reactions involving **NHC**–silver(1) halide complexes. The solvent was removed *in vacuo*, and the resulting solid dissolved in a minimum of CH₂Cl₂ and applied to a silica gel column. Elution and workup afforded two compounds, namely red crystals of **2** and scarlet crystals of **3**.

¹H and ¹³C{¹H} NMR solution studies on the *red* crystalline solid material **2** revealed the presence of a symmetrical **IMes** ligand. IR solution studies on a hexanes solution of **2** indicated the presence of seven v(CO) bands. Curiously, elemental analysis and LSIMS (P⁺ 1299.9 *m/z*) were consistent with the incorporation of [(**IMes**)AgCl] into the cluster, with concomitant loss of acetonitrile. In order to determine the atom connectivity we again used crystallographic techniques. Single crystals of **2** were grown and the results of the study are shown in Fig. 2.

As shown in the figure, the Ag–C bond is maintained in **2**, but the Ag–Cl bond has been cleaved. Two new Ag–Os interactions are formed, leading to a rare **NHC** hetero-bimetallic complex. The silver–carbon bond distance 2.120(12) Å, is longer than in the [(**IMes**)AgCl], 2.056(7) Å.⁶ The chloride atom was incorporated into a bridging position within the cluster such that the complex can be formulated as $[Os_3(\mu-Cl)(CO)_{10}(\mu-AgIMes)]$. Complex **2** is structurally related to $[Os_3(CO)_{10}(\mu-PPh_2)(\mu-AgP(C_6H_5)_3]$, which was prepared in a multistep procedure,⁷ but the preparation of this class of bimetallic butterfly complex is best achieved using the synthetic methodology used in our current report.

Finally, ¹H solution NMR on the *scarlet* crystalline solid material **3** revealed the presence of [IMes–H]⁺. IR solution studies



on a dichloromethane solution indicated the presence of six v(CO) bands. Once again, X-ray crystallographic techniques were necessary to confidently assign the atom connectivity in **3**. Single crystals of **3** were grown and the results of the study are shown in Fig. 3. The results clearly show that the solid is composed of discrete **[IMes–H]** ions and the new complex anion {[Os₃(μ -Cl)(CO)₁₀]₂Ag}.



Fig. 3 ORTEP view of the anionic component of 3. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Os(2)-Cl 2.462(7), Os(1)-Cl 2.455(6), Ag-Os(2) 2.902(1), Ag-Os(1) 2.860(1), Os(2)-Os(1) 2.781(1), Os(2)-Os(3) 2.858(1), Os(1)-Os(3) 2.858(1). Selected bond angles (°): Os(1)-Cl-Os(2) 68.86(16), Os(1)-Ag-Os(2) 57.71(3).

This anion was confirmed by the observation of a major ion detected by LSIMS studies (P⁺ 1883.4 m/z) and elemental analysis on the bulk sample was in accord with this formulation. Formation of the imidazolium species suggests the presence of water in the reaction vessel, but repeated experiments to generate compounds **2** and **3** under rigorous conditions resulted in similar isolated yields,

thus suggesting abstraction of $H^{\scriptscriptstyle +}$ from another source, such as $CH_2Cl_2.$

Compounds 2 and 3 represent unusual cases in NHC transfer reactions.³ In compound 2 it appears that facile insertion into the Ag–Cl bond can occur, and in the case of 3, anion exchange can occur with $[(IMes)_2Ag]^+[AgCl_2]^-$, a species that is available due to a dynamic equilibrium with $[(IMes)AgCl].^8$ We suggest that $[AgCl_2]^-$ ion reacts with the trinuclear cluster in such a way as to lead to its complete incorporation into 3.

The reaction of **NHC**-silver(I) chloride compounds with Group 4 metals containing Lewis acids have been shown to transfer the chloride ion to yield complex anions and the well known $[(IMes)_2Ag]^+$ ion.⁸ In the case discussed in *this* paper, incorporation of *both silver* and *chloride* groups into the metal cluster is most likely the result of the large soft late transition metal centres (osmium) providing a large source of electron density to complex the AgCl fragment. It is also possible that the steric constraints imposed by the open edge of the triangular cluster may have prevented transmetallation.

The use of NHC-silver(I) halides in transmetallation reactions involving a variety of metallic reagents has been well documented,³ however the results of the current study clearly suggest a word of caution: while NHC-silver(I) halide complexes are widely used, their chemistry is often complex. The molecules themselves engage in complex equilibria, involving ionic species as well as free carbenes,9 and in this report we show that non-classical reactions can occur. These results suggest that clean or efficient transmetallation reactions may not occur in all cases and in situ reactions involving silver(I) halides should be approached with caution as Ag containing products or intermediates may persist. The ability of silver(I) halides to form hetero-bimetallic species like 2 and 3 provides evidence for a new synthetic use for NHC-silver(I) halide complexes and is a synthetically attractive alternative to pyrolysis approaches to bimetallic species, which are often plagued with decomposition problems.

Acknowledgements

Funding was provided by the Natural Sciences and Engineering Council of Canada (NSERC) through the Discovery Grants Program to J. A. C. C. and R. K. P. J. A. C. C. acknowledges support from the Canada Research Chairs Program, the Canadian Foundation for Innovation and the Nova Scotia Research and Innovation Trust.

Notes and references

‡ General considerations: Care should be exercised when working with osmium carbonyls due to health and exposure risks. Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Solvents were thoroughly dried before use.¹⁰

§ Synthetic procedures and selected characterisation data: 1: $[Os_3(\mu-H)(\mu-Cl)(CO)_9(IMes)]$: To a Carius tube was added (160 mg, 0.19 mmol) $Os_3(\mu-H)_2(CO)_{10}$, (84 mg, 0.19 mmol) [(IMes)AgCl])], CH_2Cl_2 (20 mL) and hexanes (30 mL). The reaction vessel was degassed three times by freeze–pump–thaw methods and the purple reaction mixture placed in an oil bath overnight at 60 °C. The following morning the reaction vessel was removed from heat and the solution cooled to room temperature. The reaction vessel contained an orange–yellow solution and a small amount of dark solid was present at the bottom of the vessel. The solvent was removed *in vacuo* and the remaining solid dissolved in a minimum of CH_2Cl_2 and

applied to a silica gel column. Elution under a 30% solution of CH₂Cl₂ to hexanes afforded an orange-yellow band of 1. The resulting solid was recrystallised from a concentrated hot hexanes and toluene solution to afford 1 as orange-red crystals, (41 mg, 19%). Other bands were also eluted and these correspond to $Os_3(\mu-H)_2(CO)_{10}$ and $Os_3(CO)_{12}$ as determined by infrared spectroscopy. IR (in hexanes) v(CO): 2093m, 2051s, 2012vs, 2002s, 1990w, 1976m, 1971m, 1939m cm⁻¹. ¹H NMR (500 MHz, 295 K, CD₂Cl₂) δ -13.28 [s, 1H, μ -H], 2.10 [s, 6H, ortho-CH₃], 2.13 [s, 6H, ortho-CH₃], 2.36 [s, 6H, para-CH₃], 7.05 [s, 2H, meta-H], 7.07 [s, 2H, meta-H], 7.14 [s, 2H, imidazo-H]. ¹³C{1H} NMR (100.61 MHz, 295 K, CD₂Cl₂) δ 18.6 [s, ortho-CH3], 19.0 [s, ortho-CH3] 21.4 [s, para-CH3], 124.2 [s, NCC], 129.7 [s, Ar-C-3,5], 130.4 [s, Ar-C-3,5], 136.3 [s, Ar-C-2,6], 136.6 [s, Ar-C-2,6] 137.7 [s, Ar-C1,], 140.2 [s, Ar-C-4]. MS (LSIMS) 1164.1 (P+). Anal. Calc. for C₃₀H₂₅ClN₂O₉Os₃: C, 30.96; H, 2.17; N, 2.41. Found: C, 30.93; H, 2.14; N, 2.47. 2: [Os₃(µ-Cl)(CO)₁₀(µ-AgIMes)] was prepared by literature methods. To a Schlenk tube was added [Os₃(CO)₁₀(CH₃CN)₂] (101 mg, 0.11 mmol), [(IMes)AgCl] (49 mg, 0.11 mmol) and dry CH_2Cl_2 (30 mL). The resulting reaction mixture was allowed to stir at room temperature for 2 h. The reaction progress was followed by IR spectroscopy and the disappearance of bands in the CO stretching region associated with [Os₃(CO)₁₀(CH₃CN)₂], specifically 2023 cm⁻¹. An orange-red solution resulted and appeared to be completely reacted by IR spectroscopy. The solvent was removed under vacuum and the resulting solid dissolved in a minimum of CH2Cl2 and applied to a silica gel column. Elution under a hexanes and CH₂Cl₂ solvent system afforded two bands. An orange band eluted under 20% dichloromethane had the solvent removed and the resulting solid was recrystallised from a concentrated hexanes solution to afford 2 as red crystals (49 mg, 35%). A second deep red band eluted under 100% dichloromethane, the solvent was removed and the resulting solid was recrystallised from a concentrated dichloromethane solution to afford **3** as scarlet crystals (15 mg, 13%). **2**: IR (in hexanes) v(CO): 2092w, 2036vs, 2010s, 2003m, 1981w, 1974m, 1951m cm⁻¹. ¹H NMR (400 MHz, 295 K, CDCl₃) δ 1.83[s, 12, ortho-CH₃], 2.11 [s, 6H, para-CH₃], 6.76 [s, 4H, meta-H], 6.89 [d, 2H, imidazo-H]. ¹³C{¹H} NMR (100.61 MHz, 295 K, CD₂Cl₂) δ 17.6 [s, ortho-CH₃], 21.4 [s, para-CH₃], 122.6 [d, NCC], 129.8 [s, Ar-C-3,5], 134.9 [s, Ar-C-2,6], 135.4 [s, Ar-C1,], 139.7 [s, Ar-C-4]; MS (LSIMS) 1297.8 (P⁺). Anal. Calc. for C₃₁H₂₆ClAgN₂O₁₀Os₃: C, 28.63; H, 2.02; N, 2.15. Found: C, 28.40; H, 1.94; N, 2.01. 3: IR (in CH₂Cl₂) v(CO): 2095.5w, 2085m, 2037br,s, 2000br,m, 1976m,sh, 1959br,m cm⁻¹; ¹H NMR (500 MHz, 295 K, CD₂Cl₂) δ 2.14 [s, 12H, ortho-CH3], 2.41 [s, 6H, para-CH₃], 7.16 [s, 4H, meta-H], 7.55 [d, 2H, imidazo-H], 8.25 [s, C⁺-H] ¹³C{¹H} NMR (100.61 MHz, 295 K, CDCl₂) δ 17.7 [s, ortho-CH₃], 21.5 [s, para-CH₃], 125.7 [s, NCC], 130.8 [s, Ar-C-3,5], 134.4 [s, C1], 136.1 [s, Ar-C-2,6], 136.9 [s, Ar-C1,], 143.3 [s, Ar-C-4]; MS (LSIMS) 1883.4 (P+). Anal. Calc. for C41H25AgCl2N2O20O86: C, 22.53; H, 1.15; N, 1.28. Found: C, 22.56; H, 1.20; N, 1.40.

¶ *Crystal data: for* **1**: $C_{33,5}H_{29}CIN_2O_9O_{33}$, triclinic, space group *P*-1, *a* = 8.3651(2) Å, *b* = 10.8743(3) Å, *c* = 20.4975(7) Å, *a* = 80.968(2)°, *β* = 81.369(2)°, *γ* = 71.935(2)°, *V* = 1740.42(9) Å³, *Z* = 2, *D_c* = 2.308 Mg m⁻³, absorption coefficient = 11.056 mm⁻¹, *R*₁ (2 σ data) = 0.0344, *wR*₂ (all data) = 0.0856 GOF = 1.034.

For **2**: $C_{31}H_{24}AgClN_2O_{11}Os_3$, triclinic, space group *P*-1, *a* = 8.1388(6) Å, *b* = 12.5307(9) Å, *c* = 18.0480(10) Å, *a* = 93.746(4)°, β = 97.217(4)°, γ = 97.567(3)°, *V* = 1803.9(2) Å³, *Z* = 2, *D_c* = 2.391 Mg m⁻³, absorption coefficient = 11.195 mm⁻¹, *R*₁ (2 σ data) = 0.0540, *wR*₂ (all data) = 0.1196, GOF = 0.944.

For 3: $C_{41}H_{25}AgCl_2N_2O_{20}Os_6$, monoclinic, space group C2/c, a = 14.5755(8) Å, b = 21.6908(16) Å, c = 17.6188(11) Å, $a = 90^{\circ}$, $\beta = 106.714(3)^{\circ}$, $\gamma = 90^{\circ}$, V = 5334.9(6) Å³, Z = 4, $D_c = 2.721$ Mg m⁻³, absorption coefficient = 14.763 mm⁻¹, R_1 (2σ data) = 0.0669, wR_2 (all data) = 0.1855, GOF = 1.007. The three data sets were collected at 150 K, 150 K, and 296 K, respectively, on a Nonius Kappa-CCD diffractometer with COLLECT (Nonius B.V., 1998).

* CCDC reference numbers 629182–629184. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703071c

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- 9 To illustrate this point, a recent paper: (A. C. Sentman, S. Csihony, R. M. Waymouth and J. L. Hedrick, J. Org. Chem., 2005, 70, 2391.) reported on the catalytic behaviour of [(IMes)₂Ag][AgCl₂]. The isolated materials clearly behave as a source of catalytically active NHC, the mass spectral data suggested the presence of an ionic compound, [(IMes)₂Ag], but the solution 'H NMR spectrum was dominated by signals for IMesAgCl (see ref. 6).
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