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N-Heterocyclic Carbene−Osmium Complexes for Olefin Metathesis Reactions

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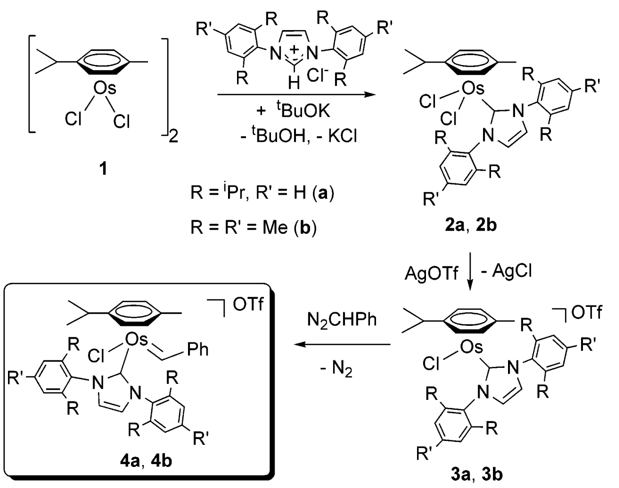
*Summary: The complexes [(η^6-p-cymene)OsCl(=CHPh)(IPr)]OTf (**4a**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene) and [(η^6-p-cymene)OsCl(=CHPh)(IMes)]OTf (**4b**; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene) have been prepared by reaction of the corresponding 16-electron compounds [(η^6-p-cymene)OsCl(NHC)]OTf (NHC = IPr (**3a**), IMes (**3b**)) with phenyldiazomethane, and their potential as initiators for olefin CM, RCM, and ROMP reactions has been explored.*

Third-row transition metals have been traditionally considered of no practical use in catalysis, since they form stronger bonds than their 3d and 4d counterparts with the ligands typically involved in the catalytic transformations.[1] Thus, in the iron triad osmium, in addition to providing a few catalysts,[2] has been used to prepare stable models of reactive intermediates proposed in reactions catalyzed by ruthenium analogues.[3]

Olefin metathesis reactions have become an efficient method for the chemo- and stereoselective formation of C−C bonds.[4] In comparison to ring-closing metathesis (RCM)[5] and ring-opening metathesis polymerization (ROMP),[6] cross-metathesis (CM)[7] remains an underrepresented area within the olefin metathesis applications. One of the most significant developments in this field has been the introduction of well-defined transition-metal alkylidene catalysts, such as the molybdenum derivative $Mo\{OC(CF_3)_2Me\}_2\{=N(C_6H_3{}^iPr_2)\}\{=CHCPh(Me)_2\}$[8] and the ruthenium compound $RuCl_2(=CHPh)(PCy_3)_2$.[9] The replacement of one phosphine in the latter by an N-heterocyclic carbene (NHC) has led to a new class of more active species, in particular for CM reactions.[5a,10] Phosphine-free derivatives containing an alkoxybenzylidene group display even higher reactivity levels toward electron-deficient substrates.[7a,11]

Scheme 1



NHC ligands are easily endowed with sterically demanding substituents on the nitrogen atom. As a result, they are able to stabilize highly reactive organometallic species, including relevant catalytic intermediates.[12] NHC−osmium complexes are extremely rare,[13] and although a few osmium catalysts for C−C coupling reactions have been reported,[14] those containing NHC ligands are unknown. We now report the preparation (Scheme 1) and characterization of the first alkylidene−osmium complexes stabilized by an NHC

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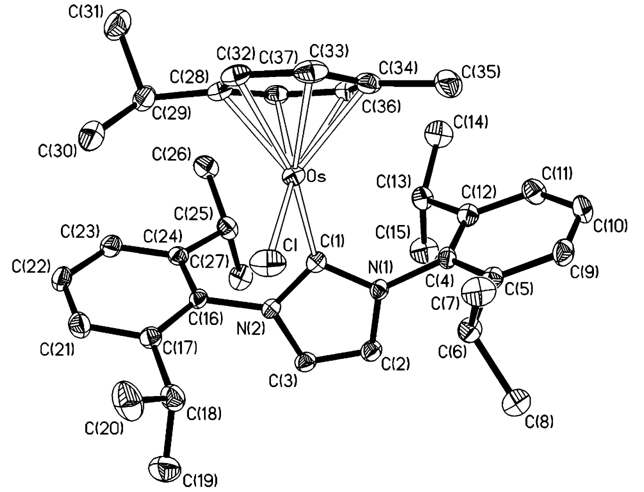

Figure 1. Molecular diagram of the cation of **3a**. Selected bond lengths (Å) and angles (deg): Os−C(1) = 2.078(2), Os−Cl = 2.2908(6), Os−C(28) = 2.161, Os−C(32) = 2.227(3); C(1)−Os−Cl = 85.96(7), C(1)−Os−C(28) = 124.97(9), C(1)−Os−C(37) = 102.04(9), C(1)−Os−C(32) = 161.81(9).

ligand. Moreover, they are efficient catalyst precursors for olefin metathesis, including CM, RCM, and ROMP reactions.

The dimer complex **1** reacts with 1,3-bis(2,6-diisopropylphenyl)imidazolylidene (IPr) and 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene (IMes) to afford the mononuclear derivatives (η^6-*p*-cymene)OsCl$_2$(NHC) (NHC = IPr (**2a**), IMes (**2b**)) in high yield. Treatment of **2a**,**b** with 1.0 equiv of silver trifluoromethanesulfonate (AgOTf) leads to the formation of the green 16-electron derivatives [(η^6-*p*-cymene)OsCl(NHC)]OTf (**3a**,**b**) in 90% and 82% yield, respectively. Their unsaturated character is supported by the X-ray structure of **3a** (Figure 1), which shows an Os−C(1) bond length of 2.078(2) Å and a C(1)−Os−Cl angle of 85.96(7)°.

The coordination vacancy in **3a**,**b** is rapidly occupied by phenylmethylene. The addition at −20 °C of 1.6 equiv of N$_2$CHPh in toluene to dichloromethane solutions of these compounds leads to the alkylidene derivatives [(η^6-*p*-cymene)OsCl(=CHPh)(NHC)]OTf (**4a**,**b**). We note that, although the diarylcarbene complexes [(η^6-Mes)OsCl(=CR$_2$)(PPh$_3$)]PF$_6$ (R = Ph, *p*-C$_6$H$_4$Me) have been isolated,[15] all attempts to obtain related compounds with an hydrogen at the carbene carbon atom have failed.[16]

Complexes **4a**,**b** are isolated as pale green solids in 78% and 72% yield, respectively. Complex **4a** was characterized by X-ray diffraction analysis. Figure 2 shows a view of its cation. The most noticeable feature of the structure is the Os−C(28) distance of 1.919(4) Å, which agrees well with those found in the half-sandwich compounds [(η^6-Mes)OsCl(=CPh$_2$)(PPh$_3$)]PF$_6$ (1.93(1) Å)[15] and Os(η^5-C$_5$H$_5$)Cl(=CHPh){P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (1.895(5) Å)[17] and supports the Os−C double-bond formulation. The Os−C(1) bond length of 2.090(3) Å is statistically identical with the related parameter in **3a**. In the ^{1}H NMR spectra of **4a**,**b**, the resonances due to the C$_\alpha$−H proton of the phenylmethylene ligand appear at 17.95 (**4a**) and 17.50 (**4b**) ppm, whereas in the ^{13}C-{^{1}H} NMR spectra the C$_\alpha$ resonances of this ligand are observed at 288.9 (**4a**) and 285.2 (**4b**) ppm, shifted about 50 ppm toward low field with regard to those found in the complexes Os(η^5-C$_5$H$_5$)Cl(=CHPh){P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (δ 234.2)[17] and Os(η^5-C$_5$H$_5$)Cl(=CHPh)(P^{i}Pr$_3$) (δ 235.0).[18]

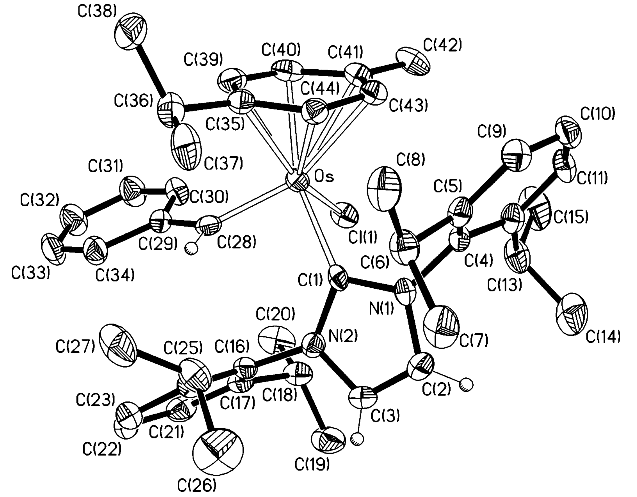

Figure 2. Molecular diagram of cation of **4a**. Selected bond lengths (Å) and angles (deg): Os−C(28) = 1.919(4), Os−C(1) = 2.090(3), Os−C(44) = 2.201(3), Os−C(41) = 2.356(4), Os−Cl = 2.3742(9); C(1)−Os−C(28) = 88.07(14), C(1)−Os−Cl = 83.74(9), C(28)−Os−Cl = 97.35(11), C(29)−C(28)−Os = 132.5(3).

Complexes **4a**,**b** are efficient catalyst precursors for the homodimerization of 1-octene and styrene, while their activities for the homodimerization of methylacrylate are poor (Table 1). With both compounds the homodimerization of the linear olefin is significantly faster than that of the aromatic substrate. According to the observed behavior, 1-octene, styrene, and methyl acrylate can be categorized as being of types I, II, and III, respectively, for CM reactions promoted by **4a**,**b**.[7b] In agreement with this classification 1-octene and styrene undergo CM reaction with methyl acrylate to afford selectively the corresponding cross products in high yield and extremely high stereoselectivity (*E*/*Z* > 98). As expected from the quite similar homodimerization of 1-octene and styrene, the CM reaction between them yields the cross product in moderate yield (71% for **4a** and 63% for **4b**) and *E*/*Z* ratios of 85 (**4a**) and 83 (**4b**).

It should be also mentioned that at the beginning of the reactions the presence of *p*-cymene is detected by GC-MS in the catalytic solution. This indicates that the 18-valence-electron precursors are activated by means of the arene decoordination, and 12-valence-electron [OsCl(=CHPh)(NHC)]$^+$ derivatives are the true initiators. In agreement with their highly unsaturated character, and previous results with ruthenium systems,[19] complex **4a**, containing the sterically more demanding IPr ligand, is more efficient than **4b**.

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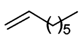
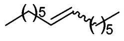
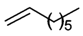
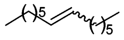
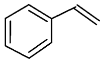
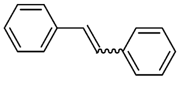
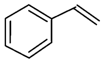
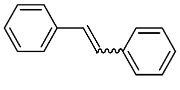
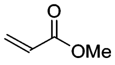
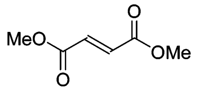
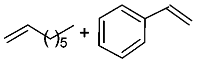
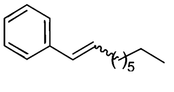
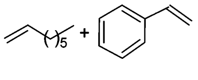
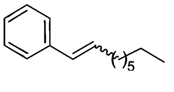
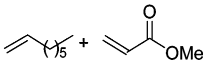
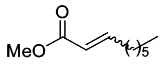
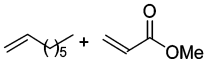
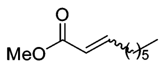
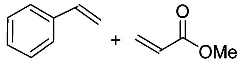
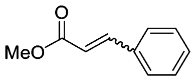
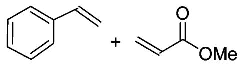
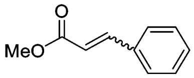
Table 1. Cross Metathesis Catalyzed by 4a,b[a]

Entry	Catalyst	Substrate	Product	T (h)	Yield(%)[b]	E/Z[b]
1	**4a**			1	75	89
2	**4b**			2	68	73
3	**4a**			14	91	>98
4	**4b**			14	49	>98
5	**4a**			24	8	-
6[c]	**4a**			5	71[d]	85
7[c]	**4b**			5	63[e]	83
8[c]	**4a**			0.5	82	>98
9[c]	**4b**			0.5	84	>98
10[c]	**4a**			4	80	>98
11[c]	**4b**			4	82	>98

[a] Performed in 1,2-dichloroethane at 60 °C with 5% mol of catalyst. [b] Determined by NMR and GC-MS. [c] Substrates are in a 1:1 ratio. [d] Stilbene (8%), 7-tetradecene (11%). [e] Stilbene (6%), 7-tetradecene (18%).

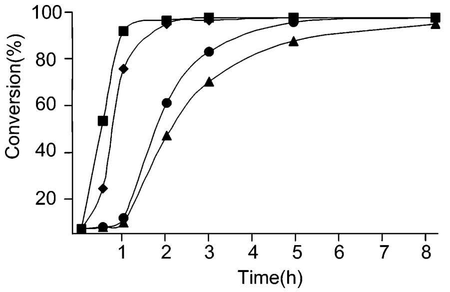


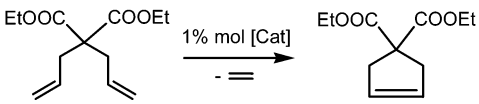
Figure 3. RCM promoted by catalysts **4a** (■, 40 °C; ●, 20 °C) and **4b** (◆, 40 °C, ▲, 20 °C).

Table 2. ROMP of Cyclooctene Mediated by 4a,b[a]

entry	catalyst	time (h)	yield (%)	$10^{-3}M_n$ [b]	PDI[c]	% cis[d]
1	**4a**	20	99	131	2.47	29
2	**4b**	20	82	115	2.35	31

[a] Performed in 1,2-dichloroethane at 60 °C. [monomer]/[catalyst] = 1000. [b] Determined by GPC in $CHCl_3$ versus polystyrene standards. [c] Polydispersity index M_w/M_n. [d] Determined by ^{13}C NMR.

Complexes **4a**,**b** are also active catalyst precursors for the RCM of 2,2-diallyl-malonic acid diethyl ester (eq 1).



(1)

Due to the decoordination of *p*-cymene from the metal center, at 20 °C, the reactions in 1,2-dichloroethane show an induction period of about 1 h, which disappears when they are performed at 40 °C (Figure 3). At this temperature, in the presence of 1% of **4a**, cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester is obtained after 1 h in 93% yield. Under the same conditions, the reaction with **4b** affords the cycloolefin in 96% yield after 2 h.[20]

Complexes **4a**,**b** promote not only CM and RCM reactions but also the ROMP of cyclooctene (Table 2). In 1,2-dichloroethane at 60 °C, and in the presence of 0.1% of metal complex, polyoctenamer with about 30% cis content is obtained after 20 h in 99% (**4a**) and 82% (**4b**) yield.

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(20) Half-sandwich *p*-cymene ruthenium complexes have also been shown to be efficient initiators for RCM and ROMP reactions, and the decoordination of the *p*-cymene ligand during the catalysis has been proposed. See: (a) Demonceau, A.; Stumpf, A. W.; Saive, E.; Noels, A. F. *Macromolecules* **1997**, *30*, 3127. (b) Fürstner, A.; Liebl, M.; Lehmann, C. W.; Piquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem. Eur. J.* **2000**, *6*, 1847. (c) Delaude, L.; Demonceau, A.; Noels, A. F. *Chem. Commun.* **2001**, 986. (d) Castarlenas, R.; Eckert M.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2576.

In conclusion, we report the preparation of the first alkylidene−osmium complexes stabilized by a NHC ligand. These compounds of formula [(η^6-*p*-cymene)-OsCl(=CHPh)(NHC)]OTf are synthons for the 12-valence-electron species $[\mathrm{OsCl({=}CHPh)(NHC)}]^+$, which are rare cases of efficient third-row initiators for olefin CM, RCM, and ROMP reactions.

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Supporting Information Available: Text giving experimental details, NMR data, and details of the crystal structure determinations; crystal data are given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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