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The First Imidazolium-Substituted Metal Alkylidene

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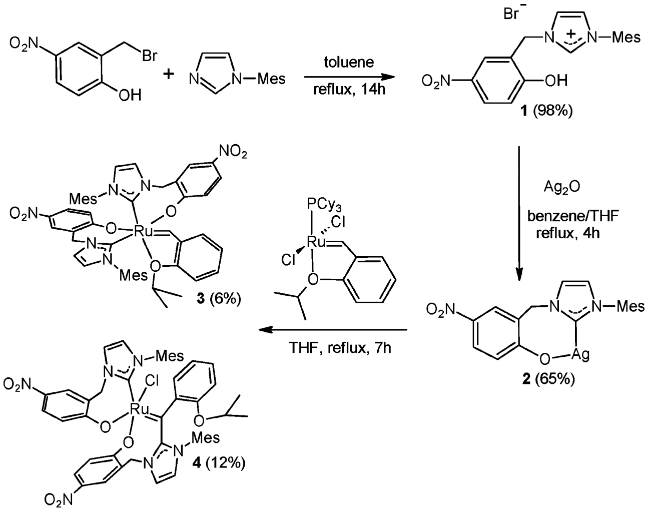
Summary: A ruthenium complex coordinated by a bidentate aryloxy-NHC ligand has offered the first example of an imidazolium-substituted metal alkylidene, an analogue of existing phosphonium alkylidenes and metal-substituted ketenes. Investigation of the molecular structure and the quantum chemically obtained electronic structure sheds light on the nature of this new compound and the bonds central to its formation.

Scheme 1. Synthesis of Complexes 3 and 4



N-heterocyclic carbenes (NHCs) are excellent and versatile dative ligands that form stable donor−acceptor complexes with a range of different metals.[1] In addition, there are also a growing number of examples where NHCs engage in bonding modes or intramolecular reactions different from those of mere spectator ligands,[2] and the carbenes show a greater tendency toward such "noninnocent" behavior than do classical dative ligands such as amines, phosphines, and carbonyl.[2] However, whereas phosphines and carbonyl form phosphonium-substituted metal alkylidenes (phosphoylides)[3−5] and metal-substituted ketenes,[6] respectively, a corresponding bond formation to alkylidene has so far not been observed for NHC. Recently, it has been discovered that phosphonium-substituted ruthenium alkylidenes such as $[(H_2IMes)Cl_2Ru{=}CH(PCy_3)]^+[B(C_6F_5)_4]^-$ are excellent catalysts[3,4] for olefin metathesis,[7] thus spurring renewed interest in transition-metal alkylidenes with substituents derived from phosphine or other soft nucleophiles.

We have set out to prepare ruthenium alkylidene complexes coordinated by bidentate aryloxy-NHC ligands and investigate their properties as olefin metathesis catalysts. In the synthesis of ligand **1** (Scheme 1), the intermediate product 1-(2,4,6-trimethylphenyl)-1*H*-imidazole was obtained by following standard procedures[8] and reacted with 2-hydroxy-5-nitrobenzyl bromide to give **1** in excellent yield. Subsequent reaction with Ag_2O resulted in the silver(I) complex **2** in good yield. In the final transmetalation step, the silver(I) salt **2** reacted slowly with the Hoveyda−Grubbs "first-generation" catalyst to produce **3** and **4**, albeit in low yields. Complexes **3** and **4** were separated by flash chromatography.

The ^1H NMR and ^{13}C NMR spectra of **3** contain H (15.90 ppm) and C resonances (297.9 ppm) typical of alkylidene hydrogen and carbon atoms, respectively, commensurate with its X-ray structure[9] (cf. the Supporting Information). The

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(1) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1291; *Angew. Chem.* **2002**, *114*, 1342.

(2) A recent example: Becker, E.; Stingl, V.; Dazinger, G.; Mereiter, K.; Kirchner, K. *Organometallics* **2007**, *26*, 1531.

(3) Dubberley, S. R.; Romero, P. E.; Piers, W. E.; McDonald, R.; Parvez, M. *Inorg. Chim. Acta* **2006**, *359*, 2658.

(4) Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6161; *Angew. Chem.* **2004**, *116*, 6287.

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(9) Data were collected using Mo Kα radiation (0.710 73 Å) at 123 K on a Bruker-AXS 2K CCD system. Compound **3** ($C_{48}H_{48}N_6O_7Ru$, M_r = 921.99) crystallizes in the monoclinic space group $P2_1/n$ with a = 14.4807(10) Å, b = 15.9232(11) Å, c = 20.1442(13) Å, β = 110.252(1)°, V = 4357.7(5) Å^3, and d_{calcd} = 1.405 g cm^{-3} for Z = 4. The structure was solved by direct methods, and least-squares refinement of the model based on 7709 (all data) and 5203 reflections ($I > 2.0\sigma(I)$) converged to a final wR2 = 0.1689 and R1 = 0.0819, respectively. Compound **4** ($C_{48}H_{47}ClN_6O_7Ru{\cdot}CH_2Cl_2$, M_r = 809.90) crystallizes in the orthorhombic space group

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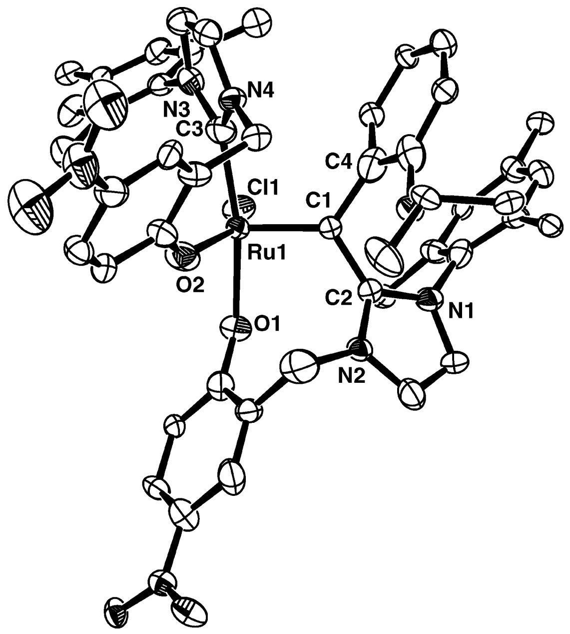


Figure 1. General view of **4** with anisotropic displacement parameters drawn at the 50% probability level. H atoms and a solvent molecule (CH_2Cl_2) have been omitted for clarity.

corresponding spectra of **4**, however, reveal the presence of an alkylidene carbon atom (244.3 ppm), but no alkylidene hydrogen atom. The X-ray structure of **4**[9] reveals an unprecedented Ru═C(Ar)(imidazolium) linkage analogous to the phosphonium-substituted metal alkylidenes[3−5] and metal-substituted ketenes;[6] see Figure 1.

The Ru1−C1 distance (186 pm) and the planar geometry of C1 (the torsion C4−C1−Ru1−C2 = 177°) suggest that **4** should be characterized as an alkylidene;[10] see Table 1. The N1−C2−N2 angle of ligand I (imidazolium bound to the alkylidene; see Scheme 2) is wider than both the N3−C3−N4 angle in ligand II (NHC bound to ruthenium; see Scheme 2) and the corresponding angles of unsaturated NHCs (imidazol-2-ylidenes) coordinated to the metal in ruthenium alkylidenes[11] but is more acute than that found in **1** or other imidazolium salts of unsaturated NHCs (Table 1). Similarly, the C2−N1 and C2−N2 distances are intermediate between C−N bond distances of NHCs and imidazolium salts. These geometric considerations suggest that the corresponding ring of ligand I of **4** has properties intermediate between those of the neutral carbene and the imidazolium ion and may be characterized as either an imidazol-2-ylidene or an imidazolium cation.

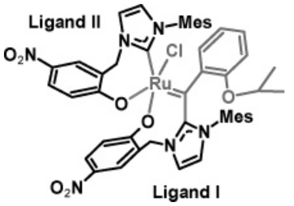
The structure of **4** as optimized using density functional theory (DFT),[13] assuming a spin singlet state, is similar to the X-ray structure (Table 1 and Figure 1).[14] This agreement, together with the observed sharp peaks of the ^1H and ^{13}C NMR spectra, strongly suggest that the complex is diamagnetic.

Table 1. Geometry Parameters and Bond Orders for 4 along with Statistical Data from Existing Ru Alkylidene Complexes[a]

	X-ray				
	this work	range[b]	mean[b]	calcd this work	Wiberg index[c]
		Bond Distances			
Ru1−C1	186	179−186	183	188	1.39
C1−C2	148			150	1.06
C1−C4	149	143−148	145	150	1.06
Ru1−Cl1	232	228−251	237	235	0.57
Ru1−O2	201	198−210	203	204	0.41
Ru1−O1	211	198−210	203	222	0.23
Ru1−C3	200	203−213	209	202	0.71
(C2−N1 + C2−N2))/2	135	132−134[d]	133[d]	138	1.25[e]
(C3−N3 + C3−N4)/2	137	134−138	136	139	1.23[e]
		Bond Angles			
Cl1−Ru1−O2	148	147−161	154	145	
C3−Ru1−O1	169			165	
N1−C2−N2	106	107−111[d]	109[d]	106	
N3−C3−N4	103	101−104	103	103	
C2−C1−C4	114			115	

[a] Bond distances in picometers and angles in degrees. [b] The reported statistics are based on 32 crystal structures of ruthenium alkylidenes.[10] [c] The calculated Wiberg bond order index.[12] [d] The reported statistics are based on 30 crystal structures of unsaturated imidazolium salts.[10] [e] Mean value for the two C−N bonds.

Scheme 2. Definition of Ligands I and II (Both Rendered in Black) in Complex 4



The Ru1−O1 bond is longer than Ru1−O2 as well as other ruthenium−oxygen bonds in alkylidene complexes,[15] suggesting an enhanced ionic character for this bond. This is corroborated by the calculated natural charges[16] for **4**, tabulated in the Supporting Information. The nitrophenyloxy moiety of ligand I is more negative ($q = -0.73$ e) than the corresponding fragment of ligand II ($q = -0.60$ e). Ru1−O1 also has the lowest Wiberg bond order index[12] of all the present ruthenium−ligand bonds, suggesting a low covalent contribution to this bond (Table 1).[12]

Whereas the C1−C2 and C1−C4 bond distances are essentially as expected for $C(sp^2)-C(sp^2)$ single bonds, and the corresponding Wiberg indices are close to unity, the nature of the Ru1−C1 bond is less clear. The Ru1−C1 distance is commensurate with a weak double bond, whereas the corresponding Wiberg index suggests a relatively low bond order: below 1.5.

$P2_12_12_1$ with $a = 10.9968(5)$ Å, $b = 15.9651(8)$ Å, $c = 26.2519(12)$ Å, $V = 4608.9(4)$ Å^3, and $d_{calcd} = 1.501$ g cm^{-3} for $Z = 4$. The structure was solved by direct methods, and least-squares refinement of the model based on 6641 (all data) and 5751 reflections ($I > 2.0s(I)$) converged to a final wR2 = 0.1036 and R1 = 0.0415, respectively. CCDC references 645473 and 645474 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(10) The Cambridge Structural Database (CSD) of Cambridge Crystallographic Data Centre (CCDC), version 5.28, updated January 2007.

(11) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236. Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T. L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.

(12) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(13) All geometry optimizations were performed using a density functional (OLYP) in combination with basis sets essentially of valence double-ζ plus polarization quality. All electronic properties were reevaluated at the optimized geometry, using a hybrid density functional (B3LYP) and basis sets that were improved in comparison to those of the geometry optimizations. See the Supporting Information for complete computational details.

(14) The geometry of **4** has also been optimized assuming a spin triplet state. The triplet is 18 kcal/mol less stable than the singlet and has a structure showing significant deviations from the X-ray diffraction structure, including a Ru1−C1 distance which is 14 pm too long.

(15) This difference between the two Ru−O distances is reflected also in the DFT-optimized geometries, although the Ru1−O1 distance is somewhat too long.

(16) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

Scheme 3. Model of 4, Used in NRT Analysis[17]

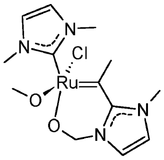


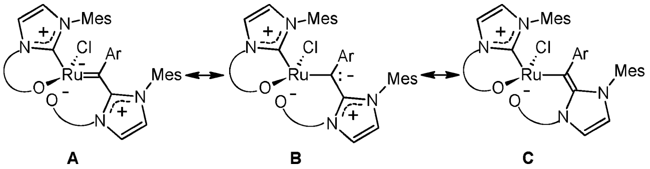
Table 2. Calculated Bond Distances and Bond Orders for the NRT Model of Complex 4[a]

bond	distance	natural bond order[b]			Wiberg index[c]
		total	covalent	ionic	
Ru1−C1	188	1.74	1.41	0.33	1.36
C1−C2	147	1.12	0.96	0.16	1.15
C1−C4	147	0.99	0.96	0.03	1.05
Ru1−Cl1	245	0.46	0.17	0.29	0.45
Ru1−O2	198	0.45	0.17	0.28	0.57
Ru1−O1	213	0.28	0.07	0.21	0.31
Ru1−C3	204	0.72	0.36	0.36	0.67

[a] Bond distances in picometers. See Scheme 3 for the structure of the model complex of **4**. [b] The natural bond order[19] is based on the resonance weights derived from NRT.[17] [c] The calculated Wiberg bond order index.[12]

In order to characterize the bonding situation in the novel compound **4** in more detail, we have performed natural resonance theory (NRT)[17] calculations on a restricted model complex of **4**, shown in Scheme 3.[18] The bond distances and Wiberg bond order indices for the model (Table 2) confirm that the coordination geometry around ruthenium and the Ru═C(Ar)(imidazolium) linkage are similar to those of the full system given in Table 1 and that the resonance theory analysis should be representative also for **4**. The natural bond order[19] (1.74) confirms that the Ru1−C1 bond should be considered a weak double bond, with some ionic contribution (0.33), represented by the three leading resonance structures **A**−**C** in Scheme 4. In addition to a covalent bond, the double bond in **A** involves an electron pair donated from C1, i.e., a dative bond, implying a formal oxidation state of +4 for ruthenium in **4**. Whereas zwitterionic and π-bound resonance structures are found to contribute little to the C1−C4 bond, the ionic contribution to C1−C2 is significant and the double-bond character is nonnegligible, resulting in a bond order higher than unity. The weakness and ionic character of the Ru−Cl and Ru−O bonds, noted above in particular for the Ru1−O1 bond, are confirmed in the resonance theory analysis.

Scheme 4. Leading Resonance Structures Describing the Ru═C(Ar)(imidazolium) Linkage, with Relative Importance A > B, C



Four-coordinate 14-electron ruthenium phosphonium alkylidenes of ruthenium, formed by phosphine attack on a protonated, electron-poor carbide carbon atom, have proven to be very active for olefin metathesis and avoid the initial phosphine dissociation step of the standard Grubbs ruthenium-based catalysts.[3] The current work shows, for the first time, that imidazolium-substituted metal alkylidenes also may be obtained. **4**, however, is a five-coordinate 16-electron complex in which the only dative ligand is an NHC that cannot be expected to dissociate easily. It is thus not surprising that preliminary investigations of **4** as an olefin metathesis catalyst have resulted in no appreciable catalytic activity.

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Supporting Information Available: Text, figures, and tables containing experimental and computational details, including synthesis and characterization data for the new compounds, and CIF files giving X-ray crystallographic data for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700590V

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(17) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593.
(18) The size of **4** precluded NRT calculations on this complex.
(19) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 610.