FULL PAPER

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Introducing Potential Hemilability into "Click" Triazoles and Triazolylidenes: Synthesis and Characterization of d^6-Metal Complexes and Oxidation Catalysis

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Hemilabile ligands are known to impart remarkable properties to their metal complexes. Herein, we present arene half-sandwich complexes of Ru^{II}, Os^{II}, and Ir^{III} with "click"-derived 1,2,3-triazole (L^1) and 1,2,3-triazol-5-ylidene (L^2) ligands containing a potentially hemilabile thioether donor. Structural elucidation of the complexes revealed localization of double bonds within the triazole in L^1 and a delocalized situation within the triazolylidene ring of L^2. For complexes with L^1, unusual coordination occurs through the less basic nitrogen "N2" of the 1,2,3-triazole. All complexes were applied for the catalytic oxidation of benzyl alcohol to benzaldehyde using *N*-methylmorpholine *N*-oxide as sacrificial oxidant. Furthermore, oxidation of diphenylmethanol to benzophenone was also achieved by using low catalyst loadings in very good yields. These are rare examples of Os^{II}–triazole, as well as of Os^{II}–triazolylidene complexes with "click"-derived ligands.

Introduction

One of the most used [3+2] cycloaddition reactions in modern chemistry is probably the Cu^I-catalyzed reaction between alkynes and azides, resulting in 1,2,3-triazoles, which constitutes the best "click reaction" known.[1] The ease and the sustainability of this reaction have turned it into a "work horse" for modern synthetic chemists. One of the fields in which substituted 1,2,3-triazoles are extensively used at the moment is coordination and organometallic chemistry.[2] Metal complexes bearing 1,2,3-triazole-based ligands have been investigated for electron-transfer systems,[3] photochemistry,[4] magnetic properties,[5] and for homogeneous catalysis.[6] Another interesting characteristic of these 1,2,3-triazoles is that they can be easily converted into 1,2,3-triazolylidenes, which belong to the class of abnormal carbenes (*a*NHC), by simple alkylation of N3 and subsequent deprotonation.[7] These compounds have also been classified as mesoionic carbenes (MIC) in recent literature.[8] Such *a*NHC's are believed to even surpass the donor abilities of their normal NHC counterparts, and to act as an electron reservoir in redox transformations (noninnocent behavior).[9] Therefore, it is not surprising that complexes bearing such triazolylidene ligands are extensively used in modern organometallics chemistry and homogeneous catalysis.[10]

Bis-chelating substituted 1,2,3-triazoles can be synthesized through Cu^I-catalyzed "click reaction" with additional heteroatom donors either on the N1 or C4 atoms (Figure 1) of the triazole ring.[2] The most widely used bis-chelating ligands of this type has been L^3 (Figure 1), where the metal atom coordinates through the more basic N3 atom of the triazole ring, and the additional donating group on the C4 atom of the 1,2,3-triazole. Alternatively, one can install the donating group on the N1 atom, and generate ligands L^4. This strategy has been successfully applied to force metal binding to the less basic N2 atom through a preferential chelating effect.[11] Since triazolylidene ligands are derived from 1,2,3-triazoles (see above), such donor atoms on N1 or C4 can also be present in the triazolylidene ligands. Ligands such as L^5 have been reported.[7,9a] However, compared with their 1,2,3-triazole counterparts L^3,

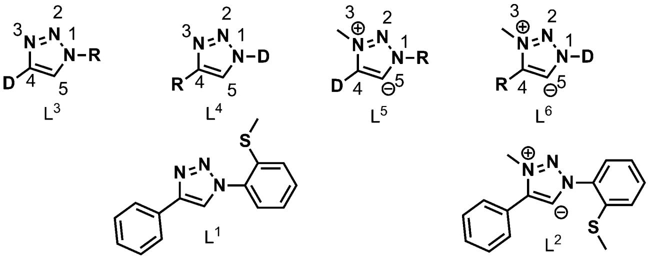

Figure 1. Potentially chelating 1,2,3-triazoles and 1,2,3-triazol-5-ylidene ligands (top), and the ligands used in this work (bottom). D denotes substituents with a heteroatom donor.

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their numbers are rather limited. To the best of our knowledge, triazolylidenes with an additional donating heteroatom on N1 (L^6) that binds to a metal center in a chelating fashion, have not been reported.

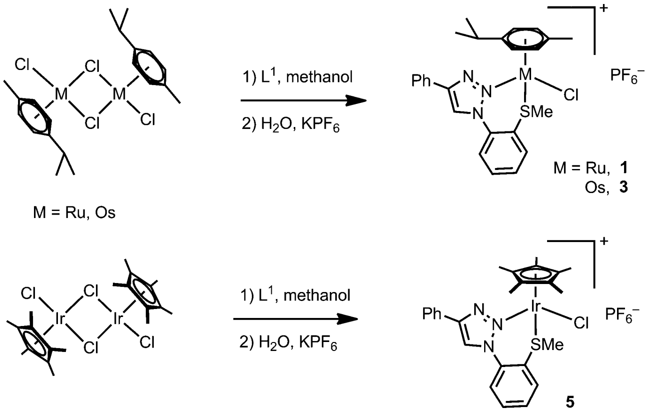
Hemilabile donating groups on ligands are often useful for generating stable catalysts in the resting state.[12] Thioether groups have been one of the most widely used hemilabile donors in organometallic chemistry.[13] Recently, we have reported on thioether functionalized ligands 1-[2-(methylthio)phenyl]-4-phenyl-1*H*-1,2,3-triazole (L^1) and 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1*H*-1,2,3-triazol-5-ylidene (L^2, Figure 1),[14] in which the donor atoms are placed on N1 of the triazole/triazolylidene ring. In these cases, we did not observe coordination of the thioether group to the metal centers. In this work, we have used the ligands L^1 and L^2 to synthesize their Ru^{II} complexes $[(Cym)Ru(L^1)Cl]PF_6$ (**1**), $[(Cym)Ru(L^2)Cl]PF_6$ (**2**), their Os^{II} complexes $[(Cym)Os(L^1)Cl]PF_6$ (**3**), $[(Cym)Os(L^2)Cl]PF_6$ (**4**) (Cym = *p*-cymene), and their Ir^{III} complexes $[(Cp^*)Ir(L^1)Cl]PF_6$ (**5**) and $[(Cp^*)Ir(L^2)Cl]PF_6$ (Cp* = pentamethylcyclopentadienyl) (**6**). In doing so, we have explored the possibility of obtaining thioether coordination in the ligands L^1 and L^2, and also looked for rare examples of Os^{II} complexes[2e] with “click”-derived substituted 1,2,3-triazole and 1,2,3-triazol-5-ylidene ligands. Herein, we present the synthesis, spectroscopic and structural characterization of the metal complexes and their use as catalysts for the oxidation of benzyl alcohol and diphenylmethanol using NMO as a sacrificial oxidant.

Results and Discussion

Synthesis and Characterization of Complexes

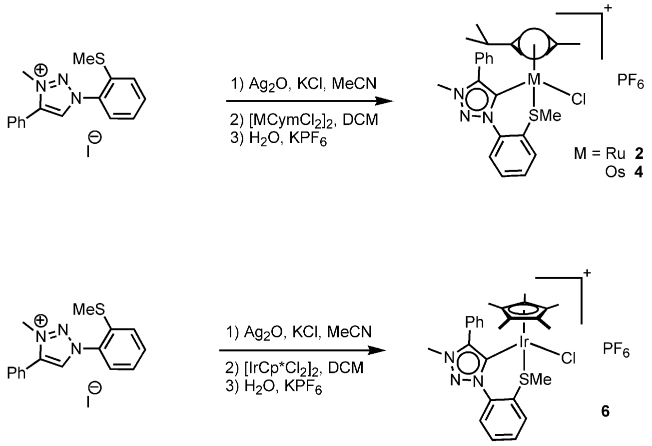
We recently reported on the synthesis of a highly effective copper(I) catalyst containing a triazolylidene ligand with an additional SMe-donor function (L^2) for the Huisgen [3+2] cycloaddition between alkynes and azides.[14] Unfortunately, several attempts at coordinating the SMe donor function to the copper center were unsuccessful. Thioether donors are known to coordinate to piano stool arene d^6 complexes when present as substituents on N-heterocyclic carbene ligands.[13a] Hence, in pursuit of realizing a thioether coordination in L^2, we wanted to synthesize half-sandwich Ru^{II}, Os^{II}, and Ir^{III} complexes with this ligand. We were also interested in the coordination mode of the non-methylated form (L^1) towards metal centers and in finding out how these two coordination modes would affect the catalytic properties of the complexes in oxidation catalysis.

Synthesis of the triazole complexes **1**, **3** and **5** was achieved by mixing the chloro-bridged dimeric metal precursors $[Ru(Cym)Cl_2]_2$, $[Os(Cym)Cl_2]_2$ or $[Ir(Cp^*)Cl_2]_2$ respectively with L^1 in methanol and subsequent stirring at room temperature overnight. Aqueous salt metathesis with KPF_6 afforded the pure complexes in good yields as yellow powders (Scheme 1). The complexes were characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry (see Exp. Sect. and Supporting Information). Whereas **5** shows a well-resolved ^1H NMR spectrum at 298 K, for **1** and **3** we observed spectra with broad peaks indicating fast transformation of rotamers within the NMR time-scale at 298 K. Heating the samples to 60 °C in methanol did not lead to complete resolution of the signals, but it clearly indicated the formation of the complexes (Figure S13 and S14, Supporting Information). Unfortunately, we were not able to record the NMR spectra in higher boiling solvents because in coordinating solvents such as CD_3CN or $[D_6]$DMSO the complexes decomposed, and the complexes were not soluble in $[D_8]$toluene. Nevertheless, we were able to identify the signal at δ = 9.29 ppm for **1** and **3** as the C–H proton of the 1,2,3-triazole ring. In contrast to the free ligand, this signal is shifted by about 1 ppm to high field. Such a shift clearly indicates binding of the ligand to the metal centers, as has been shown previously.[3h,3i] For the Ir^{III} complex **5**, all the signals were well-resolved at 298 K, and appeared at the expected positions with appropriate integrals (see the Supporting Information).



Scheme 1. Synthesis of triazole complexes **1**, **3** (top), and **5** (bottom).

Synthesis of triazolylidene complexes **2**, **4**, and **6** was achieved by following a standard transmetallation protocol (Scheme 2). The triazolium salt $[HL^2][I]$ was first reacted with basic silver(I) oxide in the presence of a chloride source (KCl) in acetonitrile (dichloromethane in the case of **2**) under exclusion of light, yielding the dicarbene silver(I) complex. Afterwards the solvent was changed to dichloromethane and the corresponding chloro-bridged dimeric metal precursors $[Ru(Cym)Cl_2]_2$, $[Os(Cym)Cl_2]_2$ or $[Ir(Cp^*)Cl_2]_2$, respectively, were added under the exclusion of light. Precipitation of AgCl indicated successful transmetallation. Filtration of AgCl and subsequent salt metathesis with aqueous KPF_6 from a methanol solution afforded the clean complexes in good yields as yellow solids. All complexes were characterized by using ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Disappearance of the C–H signal of the triazolium ring in the ^1H NMR spectra was a first indication for successful synthesis of the triazolylidene complexes. Furthermore, the observation of signals at δ = 159.9, 163.3 and 150.5 ppm for **2**, **4** and **6**, respectively, in the ^{13}C NMR spectra proved the existence of the carbene complexes (see Exp. Sect. and Supporting Information). The carbene C signal for the Cp*-Ir^{III} complex **6** appears at a much higher field compared with its Cym-Ru^{II} and Cym-Os^{II} counterparts. Furthermore, the molecular peaks for the cationic parts of all complexes (without PF_6) were observed in the ESI mass spectrum. Thus, NMR spectroscopy and mass spectrometry unambiguously demonstrate the formation of the triazole and triazolylidene complexes. These data also provide evidence for the successful synthesis of rare Os^{II} complexes[2e] with substituted 1,2,3-triazoles as well as 1,2,3-triazol-5-ylidene ligands.



Scheme 2. Synthesis of the triazolylidene complexes **2**, **4** (top), and **6** (bottom).

Crystal Structures of Complexes

Single crystals of **2** were obtained by slow diffusion of *n*-hexane into a concentrated solution of **2** in dichloromethane at room temperature. In the case of complexes **5** and **6**, slow diffusion of hexanes into a concentrated solution of the metal complex in dichloromethane at 8 °C produced X-ray quality crystals (see the Exp. Sect.). The crystallographic data are given in Table 5. All complexes display three-legged piano stool type coordination around the metal center, which is typical for half-sandwich complexes (Figure 2). The Cym ligand is bound in a η^6 mode to the Ru^{II} center in **2**, whereas the Cp* ligand binds in a η^5 mode to the Ir^{III} center in **5** and **6**. The distance of the centroid of the Cym ligand to the ruthenium center is 1.724(1) Å in **2**. The corresponding distance between the centroid of Cp* and the Ir center are 1.792(1) and 1.826(1) Å for **5** and **6**, respectively. The elongation of this distance in **6** might be due to steric repulsion with the phenyl substituent on the C2 atom of the ligand, which points towards the Cp* ligand; for complex **5** the phenyl substituent on C2 points in the opposite direction (Figure 2). The metal chloride distance is within the expected regions for all three complexes (Table 1).[15]

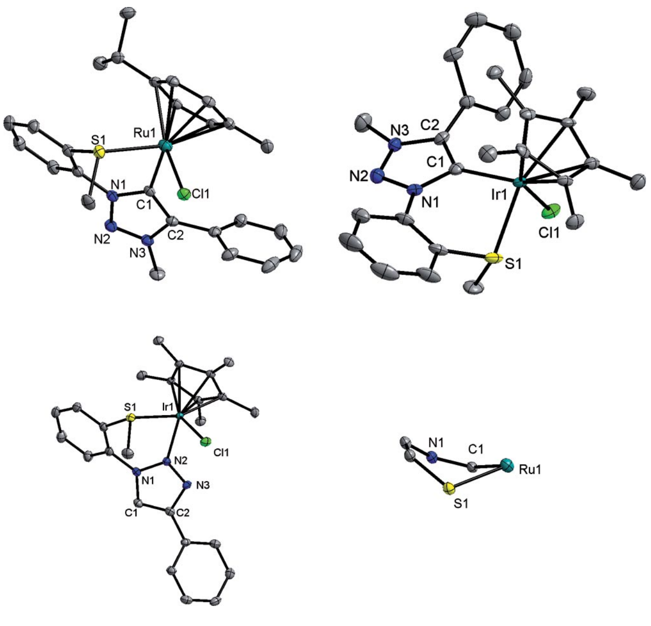


Figure 2. ORTEP plot of **2** (top left), **5** (bottom left) and **6** (top right). Ellipsoids are shown with a probability level of 50%. Hydrogen atoms and counterions have been omitted for clarity. The boat conformation around the metal center is shnown, with the example of **2** (bottom right).

Table 1. Selected bond lengths [Å].

	2	5	6
M–S1	2.351(1)	2.360(1)	2.328(2)
M–Cl1	2.413(1)	2.395(1)	2.422(2)
M–C1	2.048(2)	–	2.036(4)
M–N2	–	2.094(2)	–
N1–N2	1.343(2)	1.363(3)	1.338(5)
N2–N3	1.306(3)	1.301(4)	1.355(5)
N3–C2	1.367(3)	1.369(4)	1.355(5)
C2–C1	1.395(3)	1.370(4)	1.399(5)
C1–N1	1.382(3)	1.354(4)	1.377(5)

In **5**, the ligand L^1 acts as a chelate, with the coordinating atoms being the N2 nitrogen atom of the triazole and the sulfur atom S1 of the thioether function. The Ir–N2 distance of 2.094(2) Å, and the Ir–S1 distance of 2.360(1) Å confirm the bonding of both these donor atoms to the iridium center. Thus, chelation forces the iridium center to bind to the less basic nitrogen atom of the 1,2,3-triazole ring, as has been previously reported for metal complexes with related ligands.[11] In **5**, the donor atoms form a six-membered chelate ring at the metal center, which displays a boat-shaped conformation (Figure 2). Even though this coordination type of triazole has been observed before by others, it is the first time that such coordination has been observed for ligand L^1. The N1–N2 distance of 1.363(3) Å inside the 1,2,3-triazole ring in **5** is longer than the central N2–N3 distance of 1.301(4) Å, revealing a localized central double bond flanked by longer bonds (Table 1). The dihedral angle between the triazole ring and the thioanisole ring is 39.5(1)°, and that between the triazole ring and the phenyl ring is 41.8(1)°. Although we have not been successful in obtaining suitable single crystals of **1** and **3**, spectroscopic data and comparison to **5** points to a similar coordination of L^1 in these complexes (see Exp. Sect. and the Supporting Information).

In triazolylidene complexes **2** and **6**, the metal–carbene (C1) bond lengths are 2.048(2) and 2.036(4) Å, respectively, and are in the range of previously reported triazolylidene complexes.[15] The M–S1 distance with 2.3512(7) and 2.328(2) Å, respectively, for **2** and **6** clearly establish the binding of the thioether function to the metal center (Table 1) and is consistent with previously reported systems.[13] Similar to **5**, in both **2** and **6**, the coordinating atoms form a six-membered ring at the metal center, which displays a boat-shaped conformation (Figure 2). In the triazolylidene rings of **2** and **6**, a shrinking of the respective angles around C1 is observed in comparison to its triazole counterpart in **3** (Table 2). These data thus unambiguously establish the chelating nature of the triazolylidene ligand L^2 in complexes **2** and **6**, in which the additional heteroatom donor is attached to the nitrogen atom of the triazolylidene ring. The dihedral angles between the thioanisole ring and the triazolylidene ring in **2** and **6** are 29.9(1)° and 30.1(1)°, respectively, and those between the phenyl ring and the triazolylidene ring are 75.3(1)° and 61.9(1)°, respectively. Despite the absence of an X-ray crystal structure for the corresponding osmium complex **4**, comparison of the spectroscopic data point to an identical structure for **4**, as has been observed for **2** and **6**.

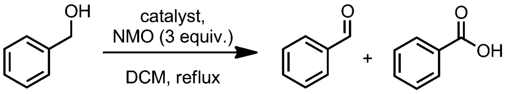
Table 2. Selected bond angles [°].

	2	**5**	**6**
C1–M–S1	84.8(1)	–	87.0(1)
N2–M–S1	–	84.9(1)	–
N1–C1–C2	101.8(2)	106.0(3)	101.7(3)
N1–N2–N3	102.9(2)	109.4(2)	103.0(3)

Catalytic Oxidation Reactions

Inexpensive and simple oxidation of small molecules is one of the major goals in organometallic chemistry, and the oxidation of alcohols is of particular interest. In recent years, *N*-methylmorpholine *N*-oxide (NMO) has emerged as a useful sacrificial oxidant for such oxidation reactions.[11m,11n] Inspired by these findings, we were interested in performing oxidation reactions with the complexes mentioned above as catalysts, and NMO as a sacrificial oxidant. For the first screening, benzyl alcohol was chosen as substrate and 1 mol-% catalyst was used with NMO in a threefold excess (see Scheme 3 and Exp. Sect.).

The conversions where investigated after 3 h reaction by ^{1}H NMR spectroscopy by using hexadecane as an internal standard. This transformation proceeded with excellent yields for the ruthenium and osmium catalysts, and afforded benzaldehyde together with its overoxidation product benzoic acid (Scheme 3 and Table 3). Looking at the conversion, certain trends can be observed for this transformation. The ruthenium complexes **1** and **2** (Table 3, entries 1 and 2) and osmium complex **3** (Table 3, entry 3) seem to be the most active catalysts for this transformation, whereas use of osmium complex **4** (Table 3, entry 4) and the iridium complexes **5** and **6** only results in moderate conversions after 3 h. Furthermore, the conversion achieved by using the substituted triazole complexes **1**, **3** and **5** were always higher than those achieved by using the corresponding triazolylidene complexes **2**, **4**, and **6**. Although the total conversion obtained by using the triazolylidene complexes **2**, **4** and **6** were lower than their respective triazole counterparts **1**, **3**, and **6**, the propensity for overoxidation to benzoic acid was markedly less for the triazolylidene-containing complexes **2**, **4** and **6** (Table 3, entries 2, 4 and 6). On comparing the three different metal centers, it is seen that with the same ligand, the osmium complexes display the highest propensity for overoxidation to benzoic acid (Table 3, entries 3 and 4). On the other hand, the iridium complexes are the most selective towards oxidation to benzaldehyde (Table 3, entries 5 and 6). Running the reactions under identical conditions with the same amount of NMO but without the catalysts resulted in no conversion into the products.



Scheme 3. Oxidation of benzyl alcohol to benzaldehyde and benzoic acid.

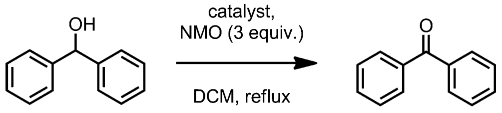
Table 3. Catalytic oxidation of benzyl alcohol under different conditions.[a]

Entry	Cat.	Loading [mol-%]	Time [h]	Conv. [%][b]	Benzaldehyde[c]	Benzoic acid[c]
1	**1**	1	3	>99	59	41
2	**2**	1	3	98	77	23
3	**3**	1	3	99	–	100
4	**4**	1	3	58	66	34
5	**5**	1	3	44	93	7
6	**6**	1	3	15	78	22
7	**1**	0.1	1	96	59	41
8	**2**	0.1	1	44	77	23
9	**3**	0.1	1	99	21	79

[a] Reaction conditions: benzyl alcohol (0.2 mmol), NMO (0.6 mmol), catalyst (1 or 0.1 mol-%), dichloromethane (4 mL), heated at reflux for 3 h or 1 h. [b] Determined by ^{1}H NMR spectroscopic analysis with hexadecane as internal standard. [c] Ratio of products given in percent.

Having established the efficiency of the complexes as catalyst at 1 mol-% loading, we next turned to the most active catalysts **1**–**3**, and decreased the catalyst loading. We lowered the catalyst loading to 0.1 mol-% and also reduced the reaction time to 1 h. As can be seen from Table 3 (entries 7–9) the trends remained similar at these catalyst loadings. The reaction with triazole complexes **1** and **3** showed nearly quantitative conversions of benzyl alcohol, whereas triazolylidene complex **2** displayed less than half the amount of product conversion compared with the reaction with 1 mol-% catalyst loading. Triazolylidene-containing complex **2** showed less overoxidation to benzoic acid (Table 3, entry 8). Moreover, on lowering the catalyst loading, the use of osmium–triazole complex **3** led to less overoxidation than with a higher catalyst loading (Table 3, entry 9).

After investigating the efficiency of the compounds reported here as catalysts for the oxidation of benzyl alcohol, which is a primary alcohol, we turned out attention to the catalytic oxidation of a secondary alcohol under the conditions detailed above. For this purpose, diphenylmethanol was chosen as substrate. One advantage of this system is the fact that overoxidation is not possible for secondary alcohols (Scheme 4 and Table 4).



Scheme 4. Oxidation of diphenylmethanol using NMO as a sacrificial oxidant.

Table 4. Catalytic oxidation of diphenylmethanol under different conditions.[a]

Entry	Catalyst	Loading [mol-%]	Time [h]	Conv. [%][b]
1	**1**	1	3	97
2	**2**	1	3	63
3	**3**	1	3	100
4	**4**	1	3	41
5	**5**	1	3	38
6	**6**	1	3	24
7	**1**	0.2	3	80
8	**2**	0.2	3	29
9	**3**	0.2	3	100
10	**3**	0.01	3	94
11	**3**	0.01	1	82

[a] Reaction conditions: diphenylmethanol (0.2 mmol), NMO (0.6 mmol), catalyst (1 or 0.2 or 0.01 mol-%), dichloromethane (4 mL), heated to reflux for 3 h or 1 h. [b] Determined by ^{1}H NMR spectroscopic analysis with hexadecane as internal standard.

Similar trends to those of the primary alcohol oxidations were observed with the secondary alcohol. The osmium complex **3**, which contains a triazole ligand, had the highest efficiency for this transformation when 1 mol-% catalyst was used (Table 4, entry 3). For all the other complexes at 1 mol-% catalyst loading, use of complexes containing a triazole ligand resulted in higher catalytic activity than use of their triazolylidene counterparts (compare entries 1 and 2, 3 and 4 or 5 and 6). We took the three most active complexes **1**, **2**, and **3** and reduced the catalyst loading to 0.2 mol-%. The catalysts retained their efficiency at this catalyst loading, and the trends observed were the same as those mentioned above (entries 7–9). Osmium complex **3** shows the highest potential for this oxidation reaction (entry 9). We were then interested in how low we could set the catalyst loading with **3** and still achieve good yields. Gratifyingly, lowering the catalyst loading to 0.01 mol-% and heating the reaction to reflux for 3 h in dichloromethane delivered 94% product conversion (entry 10). Heating the reaction to reflux for only 1 h at this catalyst loading still gave a conversion of 82% (entry 11). These results clearly demonstrate the high potency of osmium complex **3** as an oxidation catalyst.

Conclusions

We have presented here six new arene d^{6} complexes with "click"-derived 1,2,3-triazole and 1,2,3-triazol-5-ylidene ligands, both of which contain a potentially hemilabile thioether donor. In doing so, we have presented rare examples of arene–Os^{II} complexes[2e] with a "click"-derived triazole ligand, as well as with a triazolylidene abnormal carbene type of ligand. Structural characterization of selected examples has revealed the coordination of the thioether donors to the metal centers. This additional coordination, which results in chelation of the ligands to the metal centers, forces the metal centers to bind to the less basic N2 atom of the 1,2,3-triazole ring, as has been observed previously.[11] For the 1,2,3-triazol-5-ylidene ligands, these are the first examples of metal complexes in which an additional coordinating heteroatom has been incorporated into the substituents at the N1 atom of the triazolylidene ring. All complexes were investigated as catalysts for oxidations of alcohols, and most were found to be potent catalysts. A strong dependency of the outcome of the catalysis on the metal center and the ligand was observed. The osmium complexes have been shown to be superior to their ruthenium or iridium counterparts. Using the primary alcohol (benzyl alcohol), overoxidation to benzoic acid was observed, but this can be controlled to an extent by the use of an appropriate ligand or an appropriate metal center. For secondary alcohols, the catalyst loading could be reduced to only 0.01 mol-% in the case of the osmium complex **3** and still achieve high conversion after 1 h reaction. Our results thus represent a new kind of chelation for abnormal carbenes of the triazolylidene form. Furthermore, we have shown that Os^{II} complexes with "click"-derived ligands are potent oxidation catalysts. Considering the modular synthetic approach amenable to these classes of ligands, and the hitherto less explored coordination/organometallic chemistry of such hemilabile triazole/triazolylidene ligands (particularly with Os^{II}), these and related complexes are expected to find use in many catalytic processes. Current work in our laboratories is focused on some of these directions.

Experimental Section

Materials and Physical Methods: [RuCymCl$_2$]$_2$ and [IrCp*Cl$_2$]$_2$ were purchased from ABCR, and [OsCymCl$_2$]$_2$ was synthesized according to a reported procedure.[16] All the reagents were used as supplied. Ligands L^{1} and [HL^{2}][I] were synthesized according previously published methods.[14a] The solvents used for metal complex synthesis were dried and distilled under argon and degassed by common techniques prior to use. ^{1}H and ^{13}C NMR spectra were recorded with a Jeol ECS 400 spectrometer. Mass spectrometry was performed with an Agilent 6210 ESI-TOF. GC–MS analysis was performed with a Varian Saturn 2100C (column: Varian factory four capillary column VF-5ms). The presence of fluorine in the complexes (as PF_6^-) precluded the elemental analysis of these compounds. An enquiry with at least five companies supplying elemental analysis instruments forced us to conclude that no instruments are available that can be used to accurately measure compounds containing fluorine, without destroying the column of the elemental analyzer. To demonstrate the purity of these complexes, the data of all NMR spectra are reported in the Exp. Sect.

Synthesis of N^S Complexes: L^1 (53.4 g, 0.2 mmol) and the corresponding metal dimer [$(RuCymCl_2)_2$, $(OsCymCl_2)_2$, or $(IrCp^*Cl_2)_2$, 0.1 mmol] were dissolved in methanol (15 mL) and the solution was stirred at room temperature overnight. The solution was then concentrated to 1/3 of its volume and potassium hexafluorophosphate (148 mg, 0.8 mmol) was added. The mixture was stirred for 10 min, then water (80 mL) was slowly added to induce precipitation of the desired product. The yellow precipitate was filtered and washed with water, then with diethyl ether, to gain the desired complexes as yellow powders in good yields.

[Ru(Cym)Cl(L^1)] PF_6 (1): Yield 112 mg (0.164 mmol, 82%). ^{1}H NMR (400 MHz, CD_3OD; 25 °C, TMS): δ = 9.29 (s, 1 H, Triazol-5H), 8.13–8.01 (m, 3 H, Ar-H), 7.94–7.88 (m, 1 H, Ar-H), 7.87–7.78 (m, 1 H, Ar-H), 7.75–7.66 (m, 1 H, Ar-H), 7.58–7.46 (m, 3 H, Ar-H), 5.99–5.91 [m, 2 H, 2× *CH* (Cym)], 5.74 [br. s, 1 H, CH (Cym)], 5.68–5.60 [m, 1 H, *CH* (Cym)], 2.89 [br. s, 1 H, *CH* (Cym)], 2.23 [br. s, 3 H, CH_3 (Cym)], 2.10 (s, 3 H, S-CH_3), 1.34–1.26 [m, 6 H, CH_3 (Cym)] ppm. ^{13}C NMR (100 MHz, MeOD; 25 °C, TMS): δ = 151.0, 137.0 (CH_{Trz}), 133.2, 132.1, 130.8, 129.6, 129.0, 128.1, 125.8 (all Aryl-C), 109.3, 103.1 [C (Cym)], 87.9, 87.4, 86.4, 85.5 [Ar-*C*H (Cym)], 31.0 [*C*H (Cym)], 21.3 [*C*H_3 (Cym)], 20.7 (S-*C*H_3), 19.0 [*C*H_3 (Cym)], 17.1 [*C*H_3 (Cym)] ppm. MS (ESI): *m*/*z* calcd. for [$C_{26}H_{29}N_3SClRu^+$] 538.0658; found 538.0681.

[Os(Cym)Cl(L^1)] PF_6 (3): Yield 106 mg (0.136 mmol, 68%). ^{1}H NMR (400 MHz, CD_3OD; 25 °C, TMS): δ = 9.29 (s, 1 H, Triazol-5H), 8.04–7.88 (m, 4 H, Ar-H), 7.83–7.75 (m, 1 H, Ar-H), 7.73–7.65 (m 1 H, Ar-H), 7.56–7.43 (m, 3 H, Ar-H), 6.16–6.07 [m, 2 H, 2× *CH* (Cym)], 5.97–5.78 [m, 2 H, *CH* (Cym)], 2.78 [br. s, 1 H, *CH* (Cym)], 2.32 [br. s, 3 H, *CH*$_3$ (Cym)], 2.14 (s, 3 H, S-CH_3), 1.32–1.21 [m, 6 H, *CH*$_3$ (Cym)] ppm. ^{13}C NMR (100 MHz, MeOD; 25 °C, TMS): δ = 151.7, 138.6 (CH_{Trz}), 134.5, 132.9, 132.2, 131.0, 130.3, 129.2, 127.2 (all Aryl-*C*), 102.3 [*C* (Cym)], 81.3, 80.9, 79.5, 78.5 [*C*H (Cym)], 32.2 [*C*H (Cym)], 22.7 [*C*H_3 (Cym)], 22.2 [*C*H_3 (Cym)], 20.7 (S-*C*H_3), 18.3 [*C*H_3 (Cym)] ppm. MS (ESI): *m*/*z* calcd. for [$C_{25}H_{27}N_3SClOs^+$] 628.1229; found 628.1228.

[Ir(Cp*)Cl(L^1)] PF_6 (5): Yield 113 mg (0.144 mmol, 72%). ^{1}H NMR [400 MHz,$(CD_3)_2CO$; 25 °C, TMS]: δ = 9.62 (s, 1 H, Triazol-5H), 8.26–8.16 (m, 2 H, Ar-H), 8.05–8.00 (m, 2 H, Ar-H), 7.99–7.93 (m, 1 H, Ar-H), 7.89–7.83 (m, 1 H, Ar-H), 7.58–7.47 (m, 3 H, Ar-H), 2.39 (s, 3 H, S-C*H*$_3$), 1.58 (s, 15 H, Cp-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone; 25 °C, TMS): δ = 151.6, 138.0 (*C*H_{Trz}), 134.7, 134.0, 131.8, 130.7, 130.1, 129.3, 127.3, 127.2, 126.9, 123.8, 93.7, 20.4, 8.5 ppm. MS (ESI): *m*/*z* calcd. [$C_{25}H_{28}N_3SClIr^+$] 630.1322; found 630.1303.

Synthesis of the C^S Complexes: L^2 (82 mg, 0.2 mmol) was mixed under a nitrogen atmosphere with silver oxide (163 mg, 0.7 mmol) and potassium chloride (146 g, 2 mmol) and the mixture was dissolved in acetonitrile (15 mL) and stirred under exclusion of light for 2 d. The mixture was then filtered through Celite and the volatilities were removed under high vacuum. The corresponding metal dimer $[RuCymCl_2]_2$, $[OsCymCl_2]_2$, or $[IrCp^*Cl_2]_2$ (0.1 mmol) was added and the mixture was dissolved in dichloromethane (15 mL) and stirred for 2 d under the exclusion of light. The mixture was once again filtered through Celite to remove the silver chloride, which precipitated during the reaction, and all volatilities were removed under high vacuum. The crude product was then dissolved in methanol (5 mL) and the solution was stirred for 5 min before potassium hexafluorophosphate (148 mg, 0.8 mmol) was added. The mixture was stirred for 15 min and water was added slowly to cause precipitation of the desired product. The products were obtained as yellow solids.

[Ru(Cym)Cl(L^2)] PF_6 (2): L^2 (82 mg, 0.2 mmol) was mixed under nitrogen atmosphere with silver oxide (163 mg, 0.7 mmol), dissolved in dichloromethane (15 mL), and stirred under exclusion of light for 2 d. The mixture was then filtered through Celite and the metal dimer $[RuCymCl_2]_2$ (0.1 mmol) was added. The rest of the reaction was performed according to the general route, yield 63 g (0.084 mmol, 42%). ^{1}H NMR (400 MHz, CD_2Cl_2; 25 °C, TMS): δ = 8.26–8.13 (m, 1 H, Ar-H), 7.86–7.70 (m, 4 H, Ar-H), 7.62–7.53 (m, 4 H, Ar-H), 5.45 [d, *J* = 6.3 Hz, 1 H, C*H* (Cym)], 5.38 [d, *J* = 5.9 Hz, 1 H, C*H* (Cym)], 5.24–5.13 [m, 1 H, C*H* (Cym)], 5.05 [d, *J* = 6.0 Hz, 1 H, C*H* (Cym)], 4.01 (s, 3 H, N-CH_3), 2.21–1.98 [m, 4 H, S-CH_3 and C*H* (Cym)], 1.31 [s, 3 H, C*H*$_3$ (Cym)], 0.87 [d, *J* = 7.0 Hz, 3 H, C*H*$_3$ (Cym)], 0.73 [d, *J* = 6.9 Hz, 3 H, C*H*$_3$ (Cym)] ppm. ^{13}C NMR (100 MHz, CD_2Cl_2; 25 °C, TMS): δ = 159.8 (Carbene-C), 150.0 (C_{trz}-Ph), 133.2, 131.9, 130.7, 130.2, 128.6, 126.8, 126.3, 112.0 (all Aryl-*C*), 100.7 [2× *C* (Cym)], 93.5, 88.8, 87.7, 85.8 [*C*H (Cym)], 39.1 (N-*C*H_3), 22.6 [*C*H_3 (Cym)], 21.8 [*C*H_3 (Cym)], 20.3 (S-*C*H_3), 17.2 [2× *C*H_3 (Cym)] ppm. MS (ESI): *m*/*z* calcd. [$C_{26}H_{29}N_3SClRu^+$] 552.0814; found 552.0815.

[Os(Cym)Cl(L^2)] PF_6 (4): Yield 97 mg (0.124 mmol, 62%). ^{1}H NMR (400 MHz,CD_2Cl_2; 25 °C, TMS): δ = 8.22–8.17 (m, 1 H, Ar-H), 7.78–7.69 (m, 4 H, Ar-h), 7.60–7.53 (m, 4 H, Ar-H), 5.45–5.42 [m, 2 H, 2× C*H* (Cym)], 5.21 [d, *J* = 5.6 Hz, 1 H, C (Cym)], 5.09 [d, *J* = 5.6 Hz, 1 H, C*H* (Cym)], 3.99 (s, 3 H, N-C*H*$_3$), 2.19 (s, 3 H, S-CH_3), 2.05 [hept, *J* = 6.8 Hz, 1 H, C*H* (Cym)], 1.45 [s, 3 H, C*H*$_3$ (Cym)], 0.89 [d, *J* = 6.8 Hz, 3 H, C*H*$_3$ (Cym)], 0.74 [d, *J* = 6.8 Hz, 3 H, C*H*$_3$ (Cym)] ppm. ^{13}C NMR (100 MHz, CD_2Cl_2; 25 °C, TMS): δ = 163.3 (Carbene-*C*), 151.1, 144.9, 140.5, 133.8, 132.5, 132.0, 131.2, 130.5, 129.1, 127.1, 126.7, 125.1 (all Aryl-*C*), 104.6, 94.0, 85.2, 80.6, 79.5, 78.0 [all *C* (Cym)], 38.6 (N-*C*), 30.7 [*C*H (Cym)], 23.4 [*C*H_3 (Cym)], 22.6 [*C*H_3 (Cym)], 21.1 (S-*C*H_3), 17.6 [*C*H_3 (Cym)] ppm. MS (ESI): *m*/*z* calcd. [$C_{26}H_{29}N_3SClOs^+$] 642.1386; found 642.1383.

[Ir(Cp*)Cl(L^2)] PF_6 (6): Yield 127 mg (0.158 mmol, 79%). ^{1}H NMR (400 MHz, CD_2Cl_2; 25 °C, TMS): δ = 8.21–8.17 (m, 1 H, Ar-H), 7.91–7.84 (m, 2 H, Ar-H), 7.80–7.72 (m, 2 H, Ar-H), 7.62–7.50 (m, 4 H, Ar-H), 4.10 (s, 3 H, N-CH_3), 2.39 (s, 3 H, S-CH_3), 1.22 (s, 15 H, Cp-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2; 25 °C, TMS): δ = 150.5 (Carbene-*C*), 141.5, 139.7, 133.5, 132.3, 131.6, 130.8, 130.1, 128.6, 126.7, 125.5, 123.7 (all Aryl-*C*), 94.00 (Cp-*C*), 38.5 (N-*C*H_3), 22.0 (S-*C*H_3), 7.8 (Cp-*C*H_3) ppm. MS (ESI): *m*/*z* calcd. [$C_{26}H_{30}N_3SIr^+$] 644.1478; found 644.1467.

Catalysis

General Procedure for the Oxidation Catalysis: Oxidation catalysis was performed by slight modification of a reported procedure.[11n] To benzyl alcohol or diphenylmethanol (0.2 mmol), NMO (0.6 mmol) and the catalyst (1 mol-% or lower) were added anhydrous dichloromethane (4 mL). The reaction mixture was heated to reflux for 3 h or less. After cooling to room temperature, the solvent was removed and the residue was extracted in diethyl ether. After filtering this mixture over cotton, the solvent was removed again. Conversions were detected by ^{1}H NMR spectroscopic analysis with hexadecane as internal standard.

X-ray Structure Analysis: X-ray quality crystals of **1** were grown by slow diffusion of *n*-hexane into a concentrated solution of **1** in dichloromethane at room temperature. X-ray quality crystals of **5** and **6** were obtained by slow diffusion of hexane into a concentrated solution of the corresponding complex in dichloromethane at 8 °C (Table 5). Data were collected with a Bruker Smart AXS

Table 5. Structural parameters.

	2	5	6
Empirical formula	$C_{26}H_{26}ClF_6N_3PRuS$	$C_{25}H_{28}ClF_6IrN_3PS$	$C_{26}H_{30}ClF_6IrN_3PS$
M_r	697.07	775.18	789.21
Crystal system, Space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	monoclinic, Pn
a, b, c [Å]	10.604(2), 24.493(5), 10.801(2)	8.605(1), 22.776(4), 13.620(2)	10.726(5), 8.133(5), 16.339(5)
α, β, γ [°]	90, 93.028(5), 90	90, 92.848(4), 90	90, 91.562(5), 90
V [Å^3]	2801(1)	2666.8(8)	1425(1)
Z	4	4	2
Densitiy [g cm^{-3}]	1.653	1.931	1.840
F(000)	1408	1512	772
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
μ [mm^{-1}]	0.849	5.310	4.970
Crystal size	0.50 × 0.16 × 0.14	0.37 × 0.13 × 0.11	0.26 × 0.20 × 0.10
Measured reflections	41247	43514	28384
Independent reflections	8556	8117	8090
Observed [$I > 2\sigma(I)$] reflections	7840	6593	7068
R_{int}	0.0254	0.0337	0.0533
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$, S	0.0379, 0.0921, 1.174	0.0255, 0.0576, 1.092	0.0295, 0.566, 0.981
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	1.342, –0.963	2.082, –0.619	2.247, –1.412

system or a Bruker Kappa ApexII duo system. Data were collected at 100(2) or 110(2) K, respectively, using graphite-monochromated Mo-K_α radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the Smart software or the CrysAlisPro CCD software. The data were collected by standard "omega scan" or "omega+phi scan" techniques, and were scaled and reduced using Saint+software or the CrysAlisPro RED program. The structures were solved by direct methods using SHELXS-97[17] and refined by full-matrix least-squares with SHELXL-97, refining on F^2.

CCDC-952335 (for **6**), -952336 (for **5**), and -952337 (for **2**) contain the 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.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all the complexes.

Note Added in Proof (May 23, 2014): During the copy editing process of this manuscript some new complexes were reported where an additional donating group is attached to the N1 atom of the triazolylidene ring.[18]

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Catalysis for Oxidation

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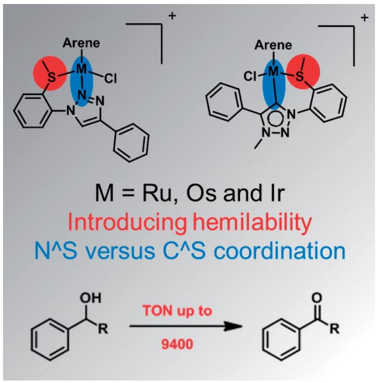
Introducing Potential Hemilability into "Click" Triazoles and Triazolylidenes: Synthesis and Characterization of d⁶-Metal Complexes and Oxidation Catalysis

Keywords: Nitrogen heterocycles / Oxidation / Carbene ligands / Ruthenium / Osmium



Ru^{II}, Os^{II}, and Ir^{III} complexes with a triazole and a triazolylidene ligand containing potential hemilabile thioether donors on the N1 atom are presented. These are rare examples of Os^{II} complexes with "click"-derived triazole and triazolylidene ligands. The new complexes (particularly the Os^{II} complexes) are shown to be potent oxidation catalysts.