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Synthesis and Structural Characterization of Cationic Rhenium(V) and Technetium(V) Dioxo Complexes Containing Four N-Heterocyclic Carbene Ligands

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Cationic dioxorhenium and dioxotechnetium complexes of the composition $[MO_2(L^1)_4]^+$ (L^1 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) have been prepared from various starting materials and studied spectroscopically and by X-ray crystallography. The metal–carbon distances range from 2.216(4) to 2.232(4) Å indicating mainly σ-bonding.

N-Heterocyclic carbenes have been established as universal ligands in the coordination and organometallic chemistry of many metals.[1,2] Transition metal complexes with these ligands possess a marked catalytic potential for various types of reactions.[3−9] Accordingly, the coordination chemistry of these highly nucleophilic species has been studied during recent years.[3,10,11] This research, however, mainly focused on compounds containing transition metals in low formal oxidation states. Only a few reports are available which refer to carbene complexes containing transition metals in high formal oxidation states,[11−13] and there is only one oxo compound, $[VOCl_3L]$ where L is 1,3-dimesitylimidazol-2-ylidene, which has been characterized by X-ray diffraction.[12] Rhenium complexes with this type of ligand, which exhibits bonding properties that do not resemble with those of "classical" Fischer-type or Schrock-type carbenes, are rare,[11,14] and complexes with technetium are hitherto unknown. In the present communication we describe synthesis and characterization of the complex cations $[ReO_2(L^1)_4]^+$ and $[TcO_2(L^1)_4]^+$, where L^1 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene.

$[ReO_2(L^1)_4]^+$ is formed by reactions of an excess of L^1 (which has been prepared from the corresponding imidazol-2-thione and potassium following a standard procedure)[15] with various rhenium(V) oxo complexes such as $[ReOCl_3(PPh_3)_2]$, $[NBu_4][ReOCl_4]$, or $[Re_2O_3Cl_4(py)_4]$ in THF (Scheme 1). The complex has been isolated as PF_6^- or ReO_4^- salts depending on the conditions applied. A typical reaction starts from 1 equiv each of $[ReOCl_3(PPh_3)_2]$ and KPF_6 and a 6-fold excess of L^1. The deposited yellow plates have a composition of $[ReO_2(L^1)_4][PF_6]$.[16] The second oxygen atom is abstracted from traces of water in the solvent, and colorless blocks of HL^1 have been isolated as a side-product and characterized by elemental analysis, IR and NMR spectroscopy, and its X-ray crystal structure.[17] Traces of water (and the ready protonation of L^1) are also the driving force for the formation of perrhenate when the reaction is performed in air. $[ReO_2(L^1)_4][ReO_4]$ precipitates from the reaction mixture at prolonged reaction times when no PF_6^- is added. Similar reactions in carefully dried solvents give dark-green solutions from which we could not yet isolate the product in crystalline form. Traces of water lead to an immediate change of the color and the formation of $[ReO_2(L^1)_4]^+$, and HL^1 is precipitated as a side product.

$[ReO_2(L^1)_4][PF_6]$ crystallizes as yellow plates. The compound is stable as a solid and in solution. The Re═O

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(1) (a) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42. (b) Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem.* **1968**, *80*, 154; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141.

(2) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J., III; Kline, M.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1991**, *113*, 9704. (c) Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523.

(3) (a) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12. (b) Herrmann, W. A. *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem., Int. Ed.* **2002**, *41*, 1294.

(4) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181.

(5) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.

(6) Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153.

(7) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(8) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.

(9) Bourissou, D.; Guerret, O.; Gabbai, F. B.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(10) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591.

(11) Herrmann, W. A.; Öfele, K.; Elison, M.; Kühn, F.; Roesky, P. W. *J. Organomet. Chem.* **1994**, *480*, C7.

(12) Abernethy, C. D.; Codd, G. M.; Spicer, M. D.; Taylor, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 1128.

(13) Cross, L.; Crane, T. W.; White, P. S.; Templeton, J. L. *Organometallics* **2003**, *22*, 548.

(14) (a) Azam, K. A.; Hossain, Md. A.; Hursthouse, M. B.; Kabir, S. E.; Malik, K. M. A.; Vahrenkamp, H. *J. Organomet. Chem.* **1998**, *555*, 285. (b) Liu, C. Y.; Chen, D. Y.; Peng, S. M.; Liu, S. T. *Organometallics* **1996**, *15*, 1055 and references therein. (c) Xue, W. M.; Chan, M. C. W.; Su, Z. M.; Cheung, K. K.; Liu, S. T.; Che, C. M. *Organometallics* **1998**, *17*, 1622.

(15) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

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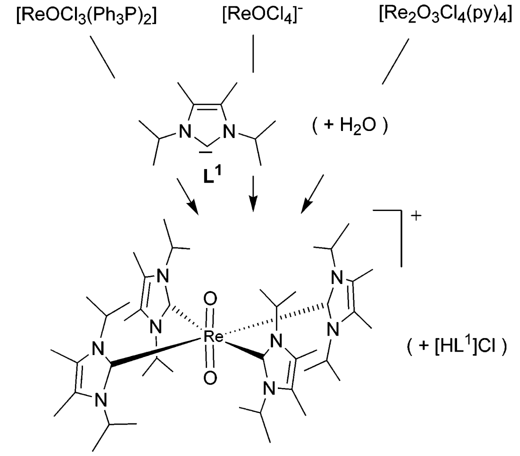
Scheme 1



vibration of the central dioxorhenium(V) unit can be detected at 775 cm^{-1}. The FAB$^+$ mass spectrum shows intense peaks for the complex cation at $m/z = 940$ and fragments which are formed by abstraction of one or two carbene ligands. The obtained NMR spectra agree with the proposed structure, and the presence of two doublets at 0.80 and 1.22 ppm in the proton spectrum indicates a hindered rotation of the methyl groups of the isopropyl substituents. The ^{13}C NMR signal of the carbene carbon atoms is found at 173.5 ppm, which is in the typical range for coordinated N-heterocyclic carbenes.[9]

The X-ray crystal structure of $[ReO_2(L^1)_4][PF_6]$ consists of well-separated complex cations and $[PF_6]^-$ anions.[19] The

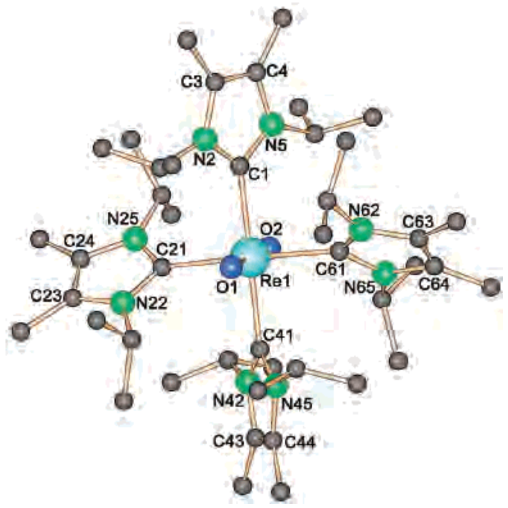


Figure 1. Molecular structure of the $[ReO_2(L^1)_4]^+$ cation together with the atomic labeling scheme.

structure of the $[ReO_2(L^1)_4]^+$ cation is shown in Figure 1. The coordination environment is a truncated octahedron with the oxo oxygen atoms in axial positions. Four L^1 ligands are bonded axially in a paddle-wheel-like arrangement. The angles between the planes of the heterocyclic rings and the least-squares plane formed from the carbene carbon atoms and Re1 range between 52.4(2)° and 57.5(2)°. These values reflect the high steric requirements of the carbene ligands and are lower by approximately 10° in the comparable ruthenium(II) complex $[RuCl_2(L^2)_4]$, where L^2 is the less bulky carbene 1,3-diethylimidazolidin-2-ylidene.[20a] Selected bond lengths and angles of the $[ReO_2(L^1)_4]^+$ cation are summarized in Table 1. The Re−O bonds are in the normal range for rhenium(V) dioxo units. The rhenium−carbon bond lengths between 2.216(4) and 2.225(4) Å are too long to suggest significant double-bond character, and, thus, σ-bonding dominates the bonding properties of the N-heterocyclic carbene in the rhenium complex under study, which allows the stabilization of the electron-deficient d^2 metal center. The extent of contributions of the structural trans influence to the weakening of the Re−C bonds cannot yet be evaluated due to the lack of complexes for comparison.

The structure of $[ReO_2(L^1)_4]^+$ is remarkable from two different points of view: (i) the coordination of four of the

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(16) $[ReO_2(L^1)_4][PF_6]$: $ReOCl_3(PPh_3)_2$ (0.925 g, 1.1 mmol) is added to a solution of L^1 (1.19 g, 6.6 mmol) in THF (20 mL) and stirred at room temperature for 2 h. The reaction mixture is filtered, and the precipitate is extracted with MeOH and filtered. To the filtrate is given a stoichiometric amount of NH_4PF_6. Concentration of the solution yields orange crystals (0.576 g, 48%). Products of the same purity and with comparable yields have been obtained from $[NBu_4][ReOCl_4]$ or $[Re_2O_3Cl_4(py)_4]$ applying the same protocol. Elemental analysis. Found: C 48.35, H 7.21, N 10.18. Calcd for $C_{44}H_{80}N_8PF_6Re$: C 48.68, H 7.43, N 10.33. IR: 3425 (w), 2974 (s), 2939 (s), 1647 (w), 1462 (m), 1385 (m), 1346 (s), 1288 (s), 1200 (m), 1134 (m), 1107 (m), 841 (s), 775 (s), 752 (w), 710 (m), 555 (m) cm^{-1}. ^{1}H NMR: $\delta = 6.09$ (m, 8 H, ^{i}PrCH, $J = 7$ Hz), 2.27 (s, 24H, CH_3), 1.22 (d, 24 H, ^{i}PrCH$_3$, $J = 7$ Hz), 0.80 (d, 12 H, ^{i}PrCH$_3$, $J = 7.3$ Hz) ppm. ^{13}C NMR: $\delta =$ 173.5 (Re*C*), 126.2 (N*C*(CH$_3$)*C*(CH$_3$)N), 50.6 (N*C*H(CH$_3$)$_2$) 21.3 (NCH(*C*H$_3$)$_2$), 20.4 (NCH(*C*H$_3$)$_2$), 10.7 (NC(*C*H$_3$)C(*C*H$_3$)N) ppm. MS: $m/z = 940$ (M$^+$), 759 (M$^+$ − L^1), 579 (M$^+$ − 2L^1), 181 (L^1). $[TcO_2(L^1)_4][TcO_4]$: $[NBu_4][TcOCl_4]$ (50 mg, 0.1 mmol) is dissolved in 5 mL of THF, and a solution of L^1 (0.11 g, 0.6 mmol) in THF is added. The mixture is filtered after stirring for 2 h at room temperature and reduced in volume to about 1 mL. Yellow plates of $[TcO_2(L^1)_4][TcO_4]$ deposit upon standing overnight at 4 °C. Yield: 25 mg (25% calculated for Tc). IR: 3441 (w), 2978 (s), 2939 (s), 1643 (w), 1462 (m), 1381 (m), 1346 (s), 1285 (w), 1200 (w), 1107 (m), 895 (s), 783 (s), 750 (w), 702 (w) cm^{-1}.

(17) $[HL^1]Cl$: colorless blocks, monoclinic, space group $P2_1/n$, $a = 11.5267$ Å, $b = 7.6452$ Å, $c = 15.0247$ Å, $\beta = 105.455°$, $Z = 4$. Bond lengths and angles in the cation are essentially the same as in previously described X-ray crystal structures for which imidazolium cations are discussed.[18]

(18) (a) Kuhn, N.; Gohner, M.; Steimann, M.; Nachtigall, C. *Z. Kristallogr., New Cryst. Struct.* **1999**, *214*, 565. (b) Kuhn, N.; Steimann, M.; Weyers, G. *Z. Kristallogr., New Cryst. Struct.* **2001**, *216*, 315. (c) Black, J. S.; Hibbs, D. E.; Hursthouse, M. B.; Jones, J.; Abdul Malik, K. M.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* **1997**, 4313. (d) Boese, R.; Blaser, D.; Kuhn, N. *Z. Kristallogr.* **1994**, *209*, 837. (e) Kuhn, N.; Walker, M, Steimann, M. *Z. Naturforsch.* **2002**, *B57*, 248. (f) Kuhn, N.; Goehner, M.; Steimann, M. *Z. Naturforsch.* **2002**, *B57*, 631.

(19) X-ray crystal structure data have been collected on a Bruker Smart CCD. Calculations have been done with SHELXS and SHELXL (G. M. Sheldrick, University of Göttingen, Germany). $[ReO_2(L^1)_4][PF_6]$: $C_{44}H_{80}N_8O_2ReF_6P$, yellow plates, triclinic, space group $P1$, $a = 12.425(3)$ Å, $b = 12.914(4)$ Å, $c = 16.605(5)$ Å, $\alpha = 103.84(1)°$, $\beta = 104.02(1)°$, $\gamma = 93.62(1)°$, $V = 2489(1)$ Å^3, $Z = 2$. $D_{calc} = 1.447$ g/cm^3, $\theta = 2.2{-}30.5°$, 26261 reflections collected, 14929 independent, $\mu = 2.529$ mm^{-1} (absorption correction SADABS, $T_{min} = 0.85848$, $T_{max} = 1.000$), 559 parameters, $R = 0.0450$, $R_w = 0.1262$. $[TcO_2(L^1)_4][TcO_4]\cdot 2.5THF$, $C_{54}H_{100}N_8O_{8.5}Tc_2$, yellow prism, triclinic, space group $P\bar{1}$, $a = 12.302(5)$ Å, $b = 16.836(5)$ Å, $c = 16.688(5)$ Å, $\alpha = 100.13(1)°$, $\beta = 98.19(1)°$, $\gamma = 106.09(1)°$, $V = 3116(2)$ Å^3, $Z = 2$. $D_{calc} = 1.272$ g/cm^3, $\theta = 1.9{-}28.0°$, 32131 reflections collected, 14919 independent, $\mu = 0.498$ mm^{-1} (no absorption correction applied), 696 parameters, $R = 0.0574$, $R_w = 0.1531$.

(20) (a) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 826. (b) Fehlhammer, W. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3370. (c) Goldberg, S. Z.; Eisenberg, R.; Miller, J. S. *Inorg. Chem.* **1977**, *16*, 1502. (d) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *Chem. Commun.* **1976**, 644. (e) Fehlhammer, W. P., Bliss, T.; Fuchs, J.; Holzmann, G. *Z. Naturforsch.* **1992**, *47b*, 79.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex Cations in $[ReO_2(L^1)_4][PF_6]$ and $[TcO_2(L^1)_4][TcO_4]$

	$[ReO_2(L^1)_4]^+$	$[TcO_2(L^1)_4]^+$
M−O1, M−O2	1.778(3), 1.782(3)	1.765(2), 1.760(3)
M−C1, M−C21	2.225(4), 2.216(4)	2.227(4), 2.232(3)
M−C41, M−C61	2.224(4), 2.231(4)	2.226(4), 2.220(3)
O1−M−O2	179.5(1)	179.8(1)
O1−M−C1, O2−M−C1	89.3(1), 91.1(2)	90.4(1), 89.5(1)
O1−M−C21, O2−M−C21	90.7(1), 89.3(1)	90.0(1), 90.0(1)
O1−M−C41, O2−M−C41	88.7(2), 90.8)1)	90.7(1), 90.6(1)
O1−M−C61, O2−M−C61	89.8(2), 90.1(1)	90.5(1), 89.5(1)

bulky ligands to one rhenium atom and (ii) the stabilization of the dioxorhenium(V) core by four carbon atoms. Both structural features are without precedence (the latter with the exception of $[ReO_2(cp)\{OB(C_6F_5)_3\}]$ which contains a η^5-bonded cyclopentadienyl ligand).[21] There are only a few structural reports of complexes where four monodentate N-heterocyclic carbenes are bonded to one metal ion, and most of them refer to electron-rich metal centers such as Pd^{2+}, Au^{3+}, Pt^{2+}, or Ru^{2+}.[20] A remarkable exception is a paramagnetic vanadium(III) complex which contains four of the anionic 3-boryl-1,4,5-trimethylimidazol-2-ylidene ligands in a distorted tetrahedral arrangement,[22] which minimizes steric restraints due to the bulky ligands.

The high formation tendency and the high stability of $[ReO_2(L^1)_4]^+$ underlines the special position of this class of ligands in the family of carbenes. Although they should formally be regarded as Fischer-type carbenes and, thus, preferably form complexes with metals in their low formal oxidation states, they show a behavior which resembles that of Schrock-type carbenes as is demonstrated with the isolation of stable rhenium(V) dioxo complexes.

The diisopropyl substituents of L^1 provide a high nucleophilic power to the carbene carbon atom, which enables the ligand to activate nitridorhenium(V) complexes. Reactions of L^1 with the common nitrido precursors $[ReNCl_2(PPh_3)_2]$ or $[ReNCl_2(PMe_2Ph)_3]$ in refluxing THF on air lead to a cleavage of the rhenium−nitrogen triple bond and to the formation of $[ReO_2(L^1)_4]^+$ under release of NH_3. This behavior is unusual for rhenium and contrasts with the results obtained for reactions of the same nitridorhenium precursors with 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (L^3) which give $[ReNCl_2(L^3)(PMe_2Ph)_2]$ and $[ReNCl(L^3)(L^3\text{-}H)_2]$, respectively.[23]

Carbene complexes of technetium are rare, and to the best of our knowledge there are only two examples of structurally characterized compounds: $[Tc({=}C{=}CHPh)Cl(DPPE)_2]$[24] and $[Tc(cp^*)(CO)_2({=}CPhOEt)]$[25] (DPPE = bis(diphenylphosphino)ethane, cp* = hexamethylcyclopentadienyl anion), which belong to the vinylidene and Fischer-carbene types. Thus, $[TcO_2(L^1)_4][TcO_4]$, which can be prepared similarly to its rhenium analogue from $[NBu_4][TcOCl_4]$ and an excess of L^1, is the first representative with N-heterocyclic carbenes. The yellow crystals of the pertechnetate salt are stable in dry air. Unlike its rhenium analogue, $[TcO_2(L^1)_4]^+$ decomposes in solution under formation of TcO_4^-. An X-ray diffraction study of $[TcO_2(L^1)_4][TcO_4]\cdot 2.5$ THF shows that the structure of the complex cation is similar to that of $[ReO_2(L^1)_4]^+$.[19] Selected bond lengths and angles are compared in Table 1. There are no significant differences between the Re−C and Tc−C bond lengths. This contrasts with the situation in $[M({=}C{=}CHPh)Cl(DPPE)_2]$ (M = Tc, Re), where the Re−C (carbene) bond is longer than that in the technetium complex by about 0.2 Å.[24] The metal atom in the $[TcO_2(L^1)_4]^+$ cation, as in the Re analogue, is effectively shielded by the isopropyl substituents. This is illustrated in Figure 2 and may explain the remarkable stability of both complexes and the fact that high oxidation states of the transition metals are effectively stabilized.

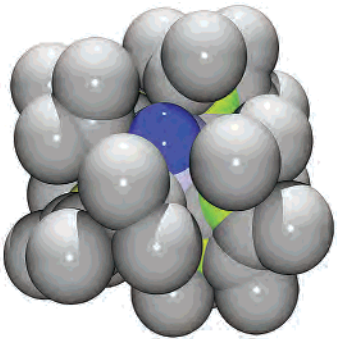

Figure 2. Space-filling model of the $[TcO_2(L^1)_4]^+$ cation illustrating the shielding of the $\{TcO_2\}^+$ core (balls represent van der Waals radii of the atoms).

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Barrado, G.; Doerrer, L.; Green, M. L. H.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1061.

(22) Wacker, A.; Chao Guo Yan; Kaltenpoth, G.; Ginsberg, A.; Arif, A. M.; Ernst, R. D.; Pritzkow, H.; Siebert, W. *J. Organomet. Chem.* **2002**, *641*, 195.

(23) Braband, H.; Abram, U. *Chem. Commun.*, in press.

(24) Burrell, A. K.; Bryan, J. C.; Kubas, G. J. *Organometallics* **1994**, *13*, 1067.

(25) Fischer, E. O.; Apostolidis, C.; Dornberger, E.; Filippou, A. C.; Kanellakopulos, B.; Lungwitz, B.; Müller, J.; Powietzka, B.; Rebizant, J.; Roth, W. *Z. Naturforsch.* **1995**, *50b*, 1382.