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Rhenium(V) Oxo Complexes with N-Heterocyclic Carbenes

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Air-stable rhenium(V) oxo complexes are formed when $[ReOCl_3(PPh_3)_2]$ is treated with N-heterocyclic carbenes of the 1,3-dialkyl-4,5-dimethylimidazol-2-ylidene type, L^R (R = Me, Et, i-Pr). Complexes of the compositions $[ReO_2(L^R)_4]^+$, $[ReOCl(L^R)_4]^{2+}$, or $[ReO(OMe)(L^R)_4]^{2+}$ can be isolated depending on the alkyl substituents at the nitrogen atoms of the ligands and the reaction conditions applied. Despite the steric overcrowding of the equatorial coordination spheres of the metal atoms by each of the four carbene ligands, stable complexes with six-coordinate rhenium atoms are obtained. Steric demands of the alkyl groups allow control of the stability of the mono-oxo intermediates. Air-stable cationic complexes of the compositions $[ReOCl(L^{Me})_4]^{2+}$, $[ReOCl(L^{Et})_4]^{2+}$, and $[ReO(OMe)(L^{Me})_4]^{2+}$ have been isolated, whereas reactions of $[ReOCl_3(PPh_3)_2]$ or other rhenium(V) precursors with the more bulky 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene ($L^{i\text{-}Pr}$) directly yield the dioxo complex $[ReO_2(L^{i\text{-}Pr})_4]^+$. X-ray structures of $[ReO_2(L^{i\text{-}Pr})_4][ReO_4]$, $[ReO_2(L^{i\text{-}Pr})_4][PF_6]$, $[ReO_2(L^{Me})_4][ReO_4]_{0.45}[PF_6]_{0.55}$, $[ReO(MeOH)(L^{Me})_4][PF_6]_2$, and $[ReOCl(L^{Et})_4][PF_6]_2$ show that the equatorial coordination spheres of the rhenium atoms are essentially planar irrespective of the steric demands of the individual carbene ligands.

Introduction

During the past four decades, there has been significant interest in N-heterocyclic carbenes (NHC) as ligands in coordination and organometallic chemistry. The first reports, published independently by Öfele and Wanzlick in 1968, are based on the in situ deprotonation of imidazolium salts by basic metal complexes.[1,2] Over 20 years later, the first crystalline N-heterocyclic carbene, 1,3-bis(adamantyl)imidazol-2-ylidene, was reported by Arduengo.[3] These nucleophilic ligands, formally Fischer-type singlet carbenes, have been mainly discussed to function solely as σ-donors.[4] A very recent report, however, claims a significant contribution of π-back-bonding interactions to the overall bonding situation in a series of copper(I), silver(I), and gold(I) NHC complexes.[5] Interest in the transition metal complexes of NHCs has been spurred by their large catalytic potential in a wide variety of reactions.[4−11] This research, however, has mainly focused on transition metal complexes in low oxidation states. There are only a few examples of N-heterocyclic carbene complexes of transition metals in high oxidation states,[12−14] and only a handful of X-ray diffraction studies of oxo complexes with this type of ligand are known in the literature.[13,16,17]

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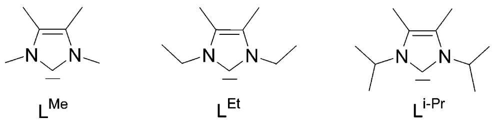
Chart 1. Heterocyclic Carbenes Used



Studies of N-heterocyclic carbene complexes of rhenium are surprisingly rare, and most of these concern carbonyl rhenium(I) complexes. In 1994, Herrmann published a report of a trioxorhenium(VII) complex with 1,3-dimethylimidazol-2-ylidene, which was studied spectroscopically but proved unstable above −20 °C and could not be structurally characterized.[12] The photochemical reaction of $Re_2(CO)_{10}$ with tetramethylthiourea gives pentarhenium clusters with bridging sulfido ligands and terminal carbonyl and tetramethyldiaminocarbene ligands.[15a] Mono- and bis(imidazolidin-2-ylidene) rhenium(I) complexes can be prepared from pentacarbonylbromorhenium and amino-phosphinimines.[15b] The bromo and one of the carbonyl ligands in the mono-(carbene) complex can be substituted with aromatic bidentate nitrogen and phosphorus donors.[15c] Nitridorhenium(V) complexes with one or two 1,3,4-triphenyl-1,2,4-triazol-5-ylidene ligands have also been reported and structurally characterized.[18] Recently, we published a short communication with the synthesis and structures of the first rhenium(V) and technetium(V) dioxo complexes with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene.[19]

Here, we present further studies of the reactions of 1,3-dialkyl substituted 4,5-dimethylimidazol-2-ylidenes, L^R with R = Me, Et, and i-Pr (see Chart 1), with oxorhenium(V) precursors, including the first X-ray crystal structures of a oxo/chloro-, oxo/methoxo-, and dioxorhenium(V) complexes all containing four N-heterocyclic carbene ligands in their equatorial coordination sphere.

Experimental Section

General Considerations. Tetrahydrofuran was dried over sodium and used freshly distilled. $[ReOCl_3(PPh_3)_2]$[20] and the 1,3-dialkyl-4,5-dimethylimidazol-2-ylidenes[21] were prepared according to literature procedures.

Infrared spectra were measured as KBr pellets on a Shimadzu FTIR-spectrometer. FAB^+ mass spectra were recorded with a TSQ (Finnigan) instrument using a nitrobenzyl alcohol matrix. Elemental analysis of carbon, hydrogen, and nitrogen were determined using an elemental analyzer from the company Heraeus (vario EL). NMR spectra were taken with a Joel 400 MHz multinucleus spectrometer.

$[ReOCl(L^{Me})_4]Cl_2$. $[ReOCl_3(PPh_3)_2]$ (300 mg, 0.36 mmol) is added to a solution of L^{Me} (268 mg, 2.16 mmol) in THF (20 mL) and stirred for 2 h. The product precipitates from the solution as a green powder (261 mg, 90%). Anal. Calcd for $C_{28}H_{48}N_8OCl_3Re$: C, 41.76; H, 6.01; N, 13.91. Found: C, 41.56; H, 6.65; N, 12.95%. IR: 3449 (s), 3149 (m), 3074 (m), 2928 (m), 1655 (s), 1639 (m), 1574 (s), 1458 (s), 1442 (s), 1369 (s), 1261 (w), 1200 (m), 1105 (m), 1094 (m), 984 (m), 908 (m), 847 (m), 762 (m), 723 (w), 690 (w), 567 (w) 486 (w) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.831$ (s, 12H, NCH_3), 3.365 (s, 12H, NCH_3), 2.179 (s, 12H, CH_3), 2.141 (s, 12H, CH_3) ppm. FAB^+ MS: $m/z = 734$, 5% B, ($[ReOCl(L^{Me})_4]^+$); 610, 5% B, ($[ReOCl(L^{Me})_3]^+$); 577, 5% B, ($[ReO(L^{Me})_3]^+$); 485, 10% B, ($[ReOCl(L^{Me})_2]^+$); 451, 5% B, ($[ReO(L^{Me})_2]^+$); 125, 100% B, ($[L^{Me}]^+$).

$[ReO(OMe)(L^{Me})_4][PF_6]_2$. Crude $[ReOCl(L^{Me})_4]Cl_2$ (260 mg, 0.32 mmol) is dissolved in MeOH, to which a methanolic solution of NH_4PF_6 is added. Concentration of the red solution yields deep red crystals (102 mg, 31%). Anal. Calcd for $C_{29}H_{51}N_8O_2P_2F_{12}Re$: C, 34.11; H, 5.04; N, 10.98. Found: C, 34.99; H, 5.69; N, 11.55%. IR: 3425 (m), 2933 (m), 1655 (m), 1462 (s), 1439 (s), 1369 (s), 1124 (s), 945 (s), 839 (vs), 738 (w), 690 (w), 557 (s) 467 (w) cm^{-1}. ^1H NMR (acetone-d_6): $\delta = 3.460$ (s, 12H, NCH_3), 3.296 (s, 12H, NCH_3), 3.235 (s, 3H, OCH_3), 2.306 (s, 12H, CH_3), 2.299 (s, 12H, CH_3) ppm. ^{13}C NMR (acetone-d_6): $\delta = 166.54$ (Re*C*), 128.41 (N*C*(CH_3)), 59.35 (ReO*C*H_3), 35.11 (N*C*H_3), 34.55 (N*C*H_3), 9.33 (C(*C*H_3)), 9.17 (C(*C*H_3)) ppm. FAB^+ MS: $m/z = 875$, 5% B, ($\{[ReO(OMe)(L^{Me})_4][PF_6]\}^+$); 730, 10% B, ($[ReO(OMe)(L^{Me})_4]^+$); 715, 10% B, ($[ReO(O)(L^{Me})_4]^+$); 606, 15% B, ($[ReO(OMe)(L^{Me})_3]^+$); 591, 15% B, ($[ReO(O)(L^{Me})_3]^+$); 481, 20% B, ($[ReO(OMe)(L^{Me})_2]^+$); 467, 100% B, ($[ReO(O)(L^{Me})_2]^+$); 365, 70% B, ($[ReO(OMe)(L^{Me})_4]^{2+}$).

$[ReO_2(L^{Me})_4][PF_6]_{0.55}[ReO_4]_{0.45}$. $[ReOCl_3(PPh_3)_2]$ (166 mg, 0.2 mmol) is added to a solution of L^{Me} (150 mg, 1.2 mmol) in THF (12 mL) and stirred for 2 h. The reaction mixture is filtered and the filtrate evaporated to dryness. The residue is washed with Et_2O, extracted with THF, and filtered. To the filtrate is added a THF solution of NH_4PF_6. The product is recovered as orange crystals (15 mg, 8%). Anal. Calcd for $C_{28}H_{48}N_8O_{5.84}P_{0.54}F_{3.25}Re_{1.46}$: C, 35.74; H, 5.36; N, 11.92. Found: C, 34.99; H, 5.69; N, 11.55. IR: 3406 (s), 2928 (m), 1653 (m), 1458 (s), 1437 (s), 1372 (s), 1186(w), 1121 (w), 1090 (w), 910 (vs) 843 (vs), 768 (vs), 723 (w), 696 (w), 557 (m) 540 (w) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.433$ (s, 24H, NCH_3, 2.207 (s, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 173.72$ (Re*C*), 125.09 (N*C*(CH_3)), 33.81 (N*C*H_3), 9.36 (C(*C*H_3)) ppm. FAB^+ MS: $m/z = 715$, 25% B, ($[ReO_2(L^{Me})_4]^+$); 591, 30% B, ($[ReO_2(L^{Me})_3]^+$); 467, 80% B, ($[ReO_2(L^{Me})_2]^+$); 125, 100%B, ($[L^{Me}]^+$).

$[ReOCl(L^{Et})_4][PF_6]$. $[ReOCl_3(PPh_3)_2]$ (83 mg, 0.1 mmol) is added to a solution of L^{Et} (94 mg, 0.6 mmol) in THF (10 mL) and stirred for 2 h. The product precipitates as its chloride salt from the solution as a crude green powder. Dissolution in methanol and addition of KPF_6 yields green crystals of the composition $[ReOCl(L^{Et})_4][PF_6]_2 \cdot 2KPF_6$ (25 mg, 17%). Anal. Calcd for $C_{36}H_{64}N_8OClReK_2P_4F_{24}$: C, 28.74; H, 4.29; N, 7.45. Found: C, 29.32; H, 4.63; N, 7.76. IR: 3422 (m), 2993 (w), 2947 (w), 2926 (w), 1655 (m), 1639 (m), 1458 (w), 1374 (m), 1340 (m), 1109 (w), 1094 (w), 993 (m), 860 (s), 844 (vs), 741 (m), 723 (w), 559 (s) cm^{-1}. ^1H NMR (DMSO-d_6): $\delta = 4.133$ (q, 8H, NCH_2, $J = 7.31$ Hz), 3.954 (q, 8H, NCH_2, $J = 7.01$ Hz), 2.072 (s, 24H, CH_3), 1.034 (t, 12H, NCH_2CH_3, $J = 7.08$ Hz), 0.913 (t, 12H, NCH_2CH_3, $J = 7.08$ Hz) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 152.67$ (Re*C*), 129.58 (N*C*(CH_3)), 14.97 (NCH_2*C*H_3), 13.95 (NCH_2*C*H_3), 9.08 (C(*C*H_3)), 8.72 (C(*C*H_3)) ppm. The signals from the methylene groups, which are expected between 35 and 45 ppm, are covered by the DMSO signal. Due to the compound's insolubility, it was impossible to measure the spectrum in a different solvent. FAB^+ MS: $m/z =$ 846, 5% B, ($[ReOCl(L^{Et})_4]^+$); 810, 5% B, ($[ReO(L^{Et})_4]^+$); 694, 5% B, ($[ReOCl(L^{Et})_3]^+$); 659, 20%B, ($ReO(L^{Et})_3^+$); 543, 5%B, ($ReOCl(L^{Et})_2^+$); 508, 20%B, ($ReO(L^{Et})_2^+$); 153, 100%B, ($(L^{Et})^+$).

$[ReO_2(L^{i\text{-}Pr})_4][ReO_4]$. $[ReOCl_3(PPh_3)_2]$ (0.083 g, 0.1 mmol) is added to a solution of L^{i-Pr} (0.110 g, 0.6 mmol) in THF (10 mL)

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Table 1. X-ray Structure Data Collection and Refinement Parameters

	$[\mathrm{ReO_2(L^{Me})_4][PF_6]_{0.55}[ReO_4]_{0.45}}\cdot$ $\mathrm{2H_2O}$	$[\mathrm{ReO_2(L^{i\text{-}Pr})_4][ReO_4]}\cdot$ 1.5THF	$[\mathrm{ReO_2(L^{i\text{-}Pr})_4][PF_6]}$	$[\mathrm{ReO(OMe)(L^{Me})_4][PF_6]_2}$	$[\mathrm{ReOCl(L^{Et})_4][PF_6]_2}\cdot$ $\mathrm{2KPF_6}$
formula	$\mathrm{C_{28}H_{48}F_{3.3}N_8O_{5.8}P_{0.55}Re_{1.45}}$	$\mathrm{C_{50}H_{92}N_8O_{7.5}Re_2}$	$\mathrm{C_{44}H_{80}F_6N_8O_2PRe}$	$\mathrm{C_{29}H_{51}F_{12}N_8O_2P_2Re}$	$\mathrm{C_{36}H_{64}ClF_{24}K_2N_8OP_4Re}$
M_w	939.27	1297.72	1084.33	1019.92	1504.68
cryst syst	monoclinic	triclinic	triclinic	monoclinic	tetragonal
a/Å	10.309(2)	12.311(5)	12.425(3)	8.459(4)	17.098(2)
b/Å	20.142(3)	16.525(5)	12.914(4)	21.184(4)	17.098(2)
c/Å	18.763(3)	16.743(5)	16.605(5)	23.314(9)	9.673(2)
α/deg	90	100.40(1)	103.84(1)	90	90
β/deg	95.63(2)	97.83(1)	104.02(1)	99.03(5)	90
γ/deg	90	106.27(1)	93.62(1)	90	90
V/Å^3	3877(1)	3152(2)	2489(1)	4126(3)	2827.8(7)
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$I4$
Z	4	2	2	4	2
D_{calc}/g cm^{-3}	1.609	1.367	1.447	1.642	1.767
μ/mm^{-1}	4.615	3.885	2.539	3.115	2.574
no. reflns	8063	39568	26261	10546	17381
no. indep	7542	18931	14929	8759	4303
no. params	416	686	559	596	180
R1/wR2[a]	0.055/0.142	0.037/0.112	0.045/0.126	0.065/0.107	0.049/0.098
GOF	1.019	1.097	1.030	0.902	0.977
device	CAD4	SMART	SMART	CAD4	SMART

[a] $R1 = |F_o - F_c|/|F_o|$; $wR2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}$.

and stirred for 6 h. The reaction mixture is filtered and the filtrate concentrated. Cooling to 0 °C overnight yields the product as orange crystals (0.035 g, 62%). Anal. Calcd for $\mathrm{C_{48}H_{88}N_8O_6Re_2}\cdot$THF: C, 45.62; H, 7.02; N, 8.87%. Found: C, 45.60; H, 6.48; N, 8.34%. IR: 3425 (w), 2974 (s), 2936 (s), 1643 (w), 1462 (m), 1381 (m), 1346 (s), 1288 (s), 1200 (m), 1134 (m), 1111 (m), 906 (s), 775 (s), 752 (w), 710 (m) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 6.012$ (br, 8H, i-PrCH), 3.674 (m, 4H, THF $\mathrm{OCH_2}$), 2.245 (s, 24H, $\mathrm{CH_3}$), 1.783 (m, 4H, THF $\mathrm{OCH_2C}H_2$), 1.198 (d, 24H, i-Pr$\mathrm{CH_3}$, $J = 6.96$ Hz), 0.777 (d, 24H, i-Pr$\mathrm{CH_3}$, $J = 7.31$ Hz) ppm. FAB$^+$ MS: $m/z = 940$, 25% B, ($[\mathrm{ReO_2(L^{i\text{-}Pr})_4}]^+$); 759, 35% B, ($[\mathrm{ReO_2(L^{i\text{-}Pr})_3}]^+$); 579, 100% B, ($[\mathrm{ReO_2(L^{i\text{-}Pr})_2}]^+$); 181, 70% B, ($[\mathrm{L^{i\text{-}Pr}}]^+$).

$[\mathrm{ReO_2(L^{i\text{-}Pr})_4][PF_6]}$. $[\mathrm{ReOCl_3(PPh_3)_2}]$ (0.925 g, 1.1 mmol) is added to a solution of $\mathrm{L^{i\text{-}Pr}}$ (1.19 g, 6.6 mmol) in THF (20 mL) and stirred 2 h. The reaction mixture is filtered, and the precipitate is extracted with MeOH and filtered. To the methanolic solution is given a stoichiometric amount of $\mathrm{NH_4PF_6}$. Concentration of the solution yields orange crystals (0.576 g, 48%). Anal. Calcd for $\mathrm{C_{44}H_{80}N_8PF_6Re}$: C, 48.68; H, 7.43; N, 10.33. Found: C, 48.35; H, 7.21; N, 10.18. 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 ($\mathrm{CDCl_3}$): $\delta = 6.092$ (m, 8H, i-PrCH, $J = 7$ Hz), 2.267 (s, 24H, $\mathrm{CH_3}$), 1.215 (d, 24H, i-Pr$\mathrm{CH_3}$, $J = 6.95$ Hz), 0.796 (d, 24H, i-Pr$\mathrm{CH_3}$, $J = 7.31$ Hz) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 173.54$ (Re*C*), 126.18 (N*C*($\mathrm{CH_3}$)*C*($\mathrm{CH_3}$)N), 50.63 (N*C*H($\mathrm{CH_3})_2$), 21.33 (NCH-($C\mathrm{H_3})_2$), 20.39 (NCH($C\mathrm{H_3})_2$), 10.69 (NC($C\mathrm{H_3}$)C($C\mathrm{H_3}$)N) ppm. FAB$^+$ MS: $m/z = 940$, 25% B, ($[\mathrm{ReO_2(L^{i\text{-}Pr})_4}]^+$); 759, 35%B, ($[\mathrm{ReO_2(L^{i\text{-}Pr})_3}]^+$); 579, 100% B, ($[\mathrm{ReO_2(L^{i\text{-}Pr})_2}]^+$); 181, 70% B, ($[\mathrm{L^{i\text{-}Pr}}]^+$).

X-ray Crystallography. The intensities for the X-ray determinations were collected on an automated single crystal diffractometer of the type CAD4 (Enraf Nonius) or on a SMART CCD (Bruker) with Mo Kα radiation ($\lambda = 0.71073$ Å). Standard procedures have been applied for data reduction and absorption correction. Structure solutions and refinements have been performed with SHELXS97 and SHELXL97.[22] More details on data collection and structure calculation are contained in Table 1.

The refinements were done with anisotropic thermal parameters for all non-hydrogen atoms unless otherwise mentioned. The positions of the hydrogen atoms were calculated using the "riding model" option of SHELXL97. Some disorders have been considered during the refinement of the structures. The phosphorus and rhenium atoms of the $[\mathrm{PF_6}]^-$ and $[\mathrm{ReO_4}]^-$ anions in $[\mathrm{ReO_2(L^{Me})_4][PF_6]_{0.55}}$-$[\mathrm{ReO_4}]_{0.45}$ occupy identical positions, and the fluorine and oxygen atoms could been assigned with the expected geometry. A free variable was introduced to determine the ratio between the anions, which was confirmed by the results of the elemental analysis of a sample of the crystals. $[\mathrm{ReOCl(L^{Et})_4][PF_6]_2}$ cocrystallized with 2 equiv of $\mathrm{KPF_6}$ per rhenium atom. The Flack parameter of the refinement of the noncentrosymmetric structure is 0.001(9). The Cl and O positions are disordered along the tetragonal axis with a ratio of 0.7/0.3. This has been taken into account during the refinement. No intermolecular K−O or K−Cl contacts have been found. Split positions have also been applied for the rhenium atom in the perrhenate counterion of $[\mathrm{ReO_2(L^{i\text{-}Pr})_4][ReO_4]}$ and the fluorine atoms of the $\mathrm{PF_6}^-$ anions in $[\mathrm{ReO(OMe)(L^{Me})_4][PF_6]_2}$. The fluorine atoms in the latter compound have been refined with isotropic thermal parameters. Additional information on the structure determinations have been deposited with the Cambridge Crystallographic Data Centre.

Results and Discussion

Reactions of 1,3-dialkyl substituted 4,5-dimethylimidazol-2-ylidenes ($\mathrm{L^R}$, R = Me, Et, i-Pr; see Chart 1) with $[\mathrm{ReOCl_3(PPh_3)_2}]$ under atmospheric conditions yield a number of mono- and dioxorhenium(V) complexes all containing four of the carbene ligands (Scheme 1). Using 6 equiv of 1,3,4,5-tetramethylimidazol-2-ylidene ($\mathrm{L^{Me}}$), $[\mathrm{ReOCl_3(PPh_3)_2}]$ can be converted to $[\mathrm{ReOCl(L^{Me})_4]Cl_2}$, which precipitates from the reaction solution as a green powder. A peak at $m/z = 734$ in the mass spectrum of the product corresponds to the complex cation $[\mathrm{ReOCl(L^{Me})_4}]^+$; the experimental isotopic pattern is consistent with that expected for a complex containing both one rhenium and one chlorine atom. Further peaks in the spectrum correspond to the loss of $\mathrm{L^{Me}}$. Less intense peaks corresponding to the loss of the chloro ligand are also

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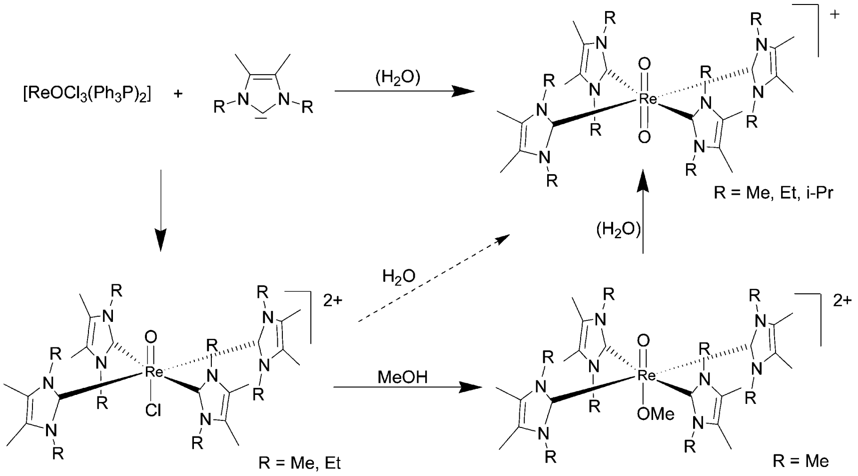
(22) Sheldrick, G. M. *SHELXS-97 and SHELXL97—programs for the solution and refinement of crystal structures*; University of Göttingen: Germany, 1997.

Scheme 1



observed. In the infrared spectrum, the peak at 984 cm^{-1} is in the range expected for the Re═O stretch of mono-oxo rhenium complexes. The ^{1}H NMR spectrum indicates the inequivalence of the two *N*-methyl groups as well as that of those bonded to carbon. This is consistent with an octahedral structure in which the four carbene ligands are coordinated equatorially around an oxo−rhenium−chloro axis. The geometry of the complex is, on the basis of NMR data, defined such that the N- and C-bound methyl groups on one side of the carbene point toward the chloro ligand and those on the other side of the carbene toward the oxo ligand. As is to be expected due to their greater proximity to the axial ligands, the signals of the *N*-methyl groups (^{1}H $\delta = 3.831$ and 3.365 ppm) are further apart than those of the C-bound methyl groups (^{1}H $\delta = 2.179$ and 2.141 ppm).

Attempts to obtain crystalline $[\text{ReOCl}(\text{L}^{\text{Me}})_4]\text{Cl}_2$ were unsuccessful. Dissolution in methanol leads to the exchange of the chloro ligand for a methoxo ligand, which is accompanied by a color change to dark red. After the addition of NH_4PF_6, deep red crystals of $[\text{ReO}(\text{OCH}_3)(\text{L}^{\text{Me}})_4][\text{PF}_6]_2$ could be isolated. The IR spectrum shows a shift of the Re═O stretch to 945 cm^{-1}. This shift indicates a weakening of the Re═O bond compared to the chloro compound and is consistent with partial double-bond character of the $\text{Re}-\text{OCH}_3$ bond, which has previously been observed for a number of *trans*-oxo/alkoxo complexes of rhenium(V).[23a] The mass spectrum of the crystals shows peaks at m/z = 830 ($[\text{ReO}(\text{OCH}_3)(\text{L}^{\text{Me}})_4][\text{PF}_6]^+$), 730 ($[\text{ReO}(\text{OCH}_3)(\text{L}^{\text{Me}})_4]^+$), and 365 ($[\text{ReO}(\text{OCH}_3)(\text{L}^{\text{Me}})_4]^{2+}$). Further fragmentation occurs through loss of carbene ligands and a methyl group. The ^{1}H and ^{13}C NMR spectra are also consistent with the proposed composition of the compound. As found for $[\text{ReOCl}(\text{L}^{\text{Me}})_4]\text{Cl}_2$, both sets of methyl groups of L^{Me} give two peaks, indicating their inequivalence, with the peaks from the N-methyl groups being further apart (^{1}H $\delta = 3.460$ and 3.296 ppm, ^{13}C $\delta = 35.11$ and 34.55 ppm) than those substituent to the carbon−carbon double bond (^{1}H $\delta = 2.306$ and 2.299 ppm, ^{13}C $\delta = 9.33$ and 9.17 ppm). This evidence suggests analogous structures for $[\text{ReOCl}(\text{L}^{\text{Me}})_4]\text{Cl}_2$ and $[\text{ReO}(\text{OCH}_3)(\text{L}^{\text{Me}})_4][\text{PF}_6]_2$. The carbene carbon signal appears at 166.5 ppm, in the expected range for bound N-heterocyclic carbenes. X-ray diffraction studies confirm the composition of the red crystals.

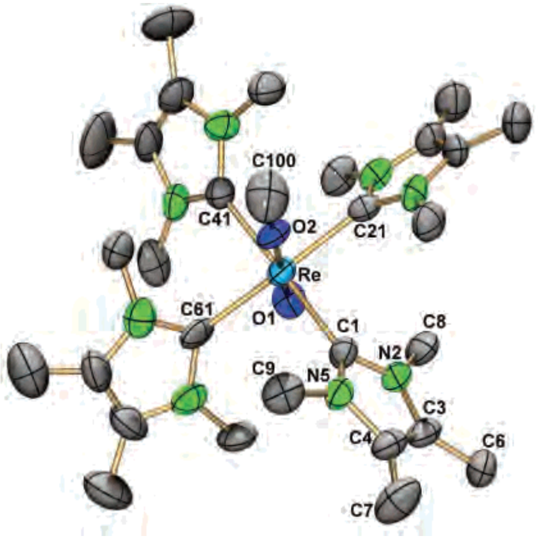


Figure 1. Ellipsoid representation[27] of the complex cation of $[\text{ReO}(\text{OMe})(\text{L}^{\text{Me}})_4][\text{PF}_6]_2$. Thermal ellipsoids represent 50% probability.

The X-ray crystal structure of $[\text{ReO}(\text{OCH}_3)(\text{L}^{\text{Me}})_4][\text{PF}_6]_2$ reveals well separated cations and anions, with the rhenium atom in a slightly distorted octahedral coordination environment. The structure of the complex cation is shown in Figure 1; selected bond lengths and angles are found in Table 2. The rhenium atom is only very slightly displaced (0.027(4) Å) from the plane formed by the carbene carbon atoms toward the oxo ligand. The heterocyclic rings are arranged in a pinwheel-like fashion around the O−Re−O axis with torsion angles to the Re−carbene plane between 44.4(4)° and 48.3(4)°. These are comparable to the angles found for the ruthenium complex $[\text{RuCl}_2\text{L}^{\text{imin}}{}_4]$ where L^{imin} is 1,3-diethyl-imidazolidin-2-ylidene.[24] The rhenium−oxo distance

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(23) (a) Abram, S.; Abram, U.; Schulz Lang, E.; Strähle, J. *Acta Crystallogr.* **1995**, *C51*, 1078 and references therein. (b) Paulo, A.; Domingos, A.; Marcalo, J.; Pires de Matos, A.; Santos, I. *Inorg. Chem.* **1995**, *34*, 2113.

(24) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 826.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[ReO(OMe)(L^{Me})_4][PF_6]_2$

Re−O1	1.695(7)	Re−O2	1.872(7)
Re−C1	2.18(1)	Re−C21	2.20(1)
Re−C41	2.20(1)	Re−C61	2.18(1)
O2−C100	1.38(2)		
O1−Re−O2	177.3(3)	O1/O2−Re−C1	91.8(4), 90.1(3)
O1/O2−Re−C21	89.6(4), 88.5(3)	O1/O2−Re−C(41)	89.6(4), 88.6(3)
O1/O2−Re−C(61)	92.7(4), 89.2(4)	C(1)−Re−C(21)	90.0(4)
C(21)−Re−C(41)	90.9(4)	C(41)−Re−C(61)	88.4(4)
C(61)−Re−C(1)	90.6(4)	C(1)−Re−C(41)	178.4(4)
C(21)−Re−C(61)	177.6(4)	Re−O−C100	173.4(8)

of 1.695(7) Å is in the expected range for mono-oxo rhenium complexes. The Re−OCH_3 distance of 1.872(7) Å is expectedly longer but reflects some double bond character as has been observed previously for a number of rhenium(V) complexes with oxo and alkoxo ligands in *trans* position.[23a] Markedly longer Re−OR bonds have been found when the alkoxo units are *cis* to the oxo unit.[23b] The long Re−carbene bonds of at or just under 2.2 Å indicate that these singlet carbene ligands function mainly as σ-donors. Although this conclusion cannot be drawn solely by a bond length consideration (also bearing in mind that the equatorial coordination sphere of the $[ReO(OMe)(L^{Me})_4]^{2+}$ cation is sterically overcrowded), a rhenium−carbon double bond with significant contributions from π-back-bonding cannot plausibly be postulated for the electron-poor d^2 system under study. This, however, cannot be ruled out for electron-rich metal ions as has recently been pointed out in a detailed study of the electronic structure of group 11 metal complexes with the polycarbene ligand 1,1,1-[tris(3-methylimidazol-2-ylidene)methyl]ethane. An analysis of the bonding situation in these complexes with the aid of the results of DHT calculations reveals in addition to the expected σ-type interactions a significant contribution of π-back-bonding. It was deduced that π-back-bonding interactions in these complexes contribute to approximate 15−30% of the complexes' overall orbital interaction energies.[5]

Another remarkable structural characteristic of the $[ReO(OMe)(L^{Me})_4]^{2+}$ cation is the nearly linear coordination of the methoxide ligand, which coordinates with a Re(1)−O(2)−C(100) angle of 173.4(8)°. This significant deviation from a bent arrangement of the Re−O−Me unit can be attributed to steric crowding due to the N-methyl substituents of the carbene ligands. The space-filling depiction of this complex (Figure 2) shows how crowded even the periphery of the complex is. This steric crowding is undoubtedly the cause of the unusual methoxy coordination angle.

Both in solution and in the solid state, $[ReO(OCH_3)(L^{Me})_4][PF_6]_2$ is stable to air and water for a few days. Standing under ambient conditions in both states for weeks or months, however, produces a color change from orange to red and the appearance of a band in the IR spectrum at 768 cm^{-1}, a frequency which is consistent with conversion to a dioxo rhenium species.

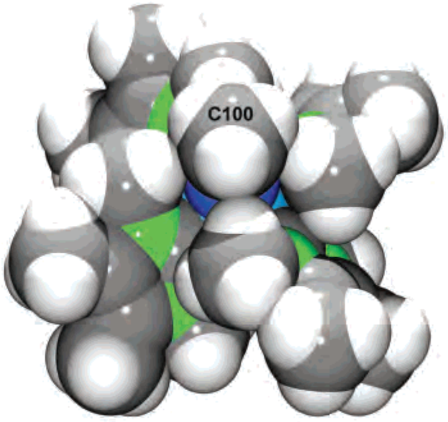

Figure 2. Space filling model of the complex cation of $[ReO(OMe)(L^{Me})_4][PF_6]_2$.

Traces of water in the solvent and the atmosphere lead to the formation of $[ReO_2(L^{Me})_4][ReO_4]$ as a side product in the reaction of L^{Me} and $ReOCl_3(PPh_3)_2$. The role of water as the source for the second oxygen atom of the dioxo unit was proven by the addition of small amount of ^{18}O-water to the reaction mixture. The formation of perrhenate, however, is related with the presence of atmospheric oxygen in the reaction mixture. Interestingly, the $[ReO_2(L^{Me})_4]^+$ cation resists air-oxidation when it is once formed. The crystalline orange complex $[ReO_2(L^{Me})_4][ReO_4]$ can be isolated from the reaction solution, and crystals suitable for X-ray diffraction studies can be obtained by recrystallization from THF with added NH_4PF_6. Solution of the crystal structure reveals a cocrystallization of the salts $[ReO_2(L^{Me})_4][ReO_4]$ and $[ReO_2(L^{Me})_4][PF_6]$ in a ratio of roughly 9:11. This mixture is confirmed by the IR spectrum, which contains strong bands at 910 and 843 cm^{-1}, corresponding to ReO_4^- and PF_6^-, respectively. The presence of the dioxo moiety is also indicated by the IR spectrum, with a strong band at 768 cm^{-1}, within the typical range for dioxorhenium complexes. In contrast to the mono-oxo species, the ^1H and ^{13}C NMR spectra give evidence for the equivalence within each of the sets of methyl groups (N- and C-substituted), as only one signal is observed for each set. The chemical shifts, however, are not significantly different from those observed for the mono-oxo complexes. The only significant difference between the NMR spectra of the mono-oxo and dioxo complexes concerns the carbene carbon atom, for which the ^{13}C chemical shift is nearly 10 ppm larger for the dioxo as for the mono-oxo complex.

X-ray diffraction studies on this mixture of salts show clearly separated cations and anions. The disordered central atoms of the counterions are both found at the same coordinates, with occupancy favoring the PF_6^- anion slightly. The complex cation (Figure 3) has a slightly distorted octahedral coordination sphere, with four equatorial carbene ligands arranged in the familiar pinwheel fashion around the *trans*-dioxo axis. The torsional angles between the plane formed by rhenium and the carbene carbon atoms and the planes of the heterocycles (45.4(4)−52.1(4)°) are of a similar magnitude to those in $[ReO(OCH_3)(L^{Me})_4][PF_6]_2$. Selected bond lengths and angles of the compound are contained in

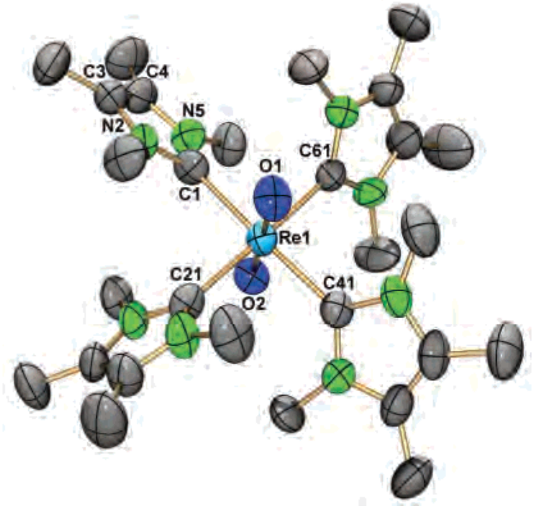

Figure 3. Ellipsoid representation[27] of the complex cation of $[ReO_2(L^{Me})_4]^+$. Thermal ellipsoids represent 50% probability.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Dioxorhenium Carbene Complexes of This Study

	$[ReO_2(L^{i-Pr})_4]$-$[ReO_4]$	$[ReO_2(LiPr)_4]$-$[PF_6]$	$[ReO_2(L^{Me})_4]$-$[PF_6]_{0.55}[ReO_4]_{0.45}$
Re1−O1	1.798(3)	1.778(3)	1.773(7)
Re1−O2	1.781(3)	1.782(3)	1.768(7)
Re1−C1	2.222(4)	2.225(4)	2.20(1)
Re1−C21	2.227(3)	2.216(4)	2.21(1)
Re1−C41	2.229(4)	2.224(4)	2.19(1)
Re1−C61	2.219(3)	2.231(4)	2.20(1)
O1−Re1−O2	180.0(2)	179.5(1)	179.4(3)
O1/O2−Re1−C1	90.5(1), 89.5(1)	89.3(1), 91.1(1)	90.2(4), 89.8(4)
O1/O2−Re1−C21	90.0(1), 90.0(1)	90.8(1), 89.3(1)	90.3(3), 89.1(3)
O1/O2−Re1−C41	90.4(1), 89.6(1)	88.7(1), 90.8(1)	89.9(4), 90.1(4)
O1/O2−Re1−C61	90.6(1), 89.4(1)	89.8(1), 90.1(1)	90.6(3), 90.0(3)
C1−Re1−C21	90.2(1)	91.8(2)	88.6(3)
C21−Re1−C41	89.9(1)	88.5(1)	93.6(4)
C41−Re1−C61	89.7(1)	89.2(1)	88.5(3)
C61−Re1−C1	90.1(1)	90.6(1)	89.3(3)
C1−Re1−C41	179.1(1)	178.1(1)	177.8(3)
C21−Re1−C61	179.3(1)	177.6(1)	177.8(4)

Table 3. The Re−carbene bond lengths are also nearly identical to those in $[ReO(OCH_3)(L^{Me})_4][PF_6]_2$, indicating a similar bonding situation. The mutual *trans*-influence of the oxo ligands leads to rhenium−oxo bonds (1.773(7) and 1.768(7) Å), which are lengthened compared to $[ReO(OCH_3)(L^{Me})_4][PF_6]_2$, but in the typical range for dioxorhenium units being slightly longer than the values in the corresponding $[ReO_2(pyridine)_4]^+$ complexes.[25]

When the analogous reaction is performed with 1,3-diethyl-4,5-dimethylimidazol-2-ylidene (L^{Et}), a similar result is observed. A green precipitate can be isolated from the brown reaction mixture. Upon solution in methanol, no color change is observed, and addition of KPF_6 yields green crystals containing the complex cation $[ReOCl(L^{Et})_4]^{2+}$. The IR spectrum of the crystals reveals a band at 993 cm^{-1}, in the expected range for the stretching frequency of a rhenium−mono-oxo bond. Also notable are very strong bands at 845 and 559 cm^{-1}. This feature suggests the presence of PF_6^- counterions. The NMR spectra of this compound show, as for $[ReOCl(L^{Me})_4]Cl_2$ and $[ReO(OCH_3)(L^{Me})_4][PF_6]_2$, split signals from the ethyl substituents, a result that is consistent with a structure in which four carbene ligands are situated in a square plane perpendicular to an O−Re−Cl axis. In contrast to the other mono-oxo compounds, a split signal from the methyl groups to the carbon−carbon double bond is not observed. It is likely that the two methyl groups are not in exactly the same chemical environment, but that the effect is too small for two separate peaks to be resolved.

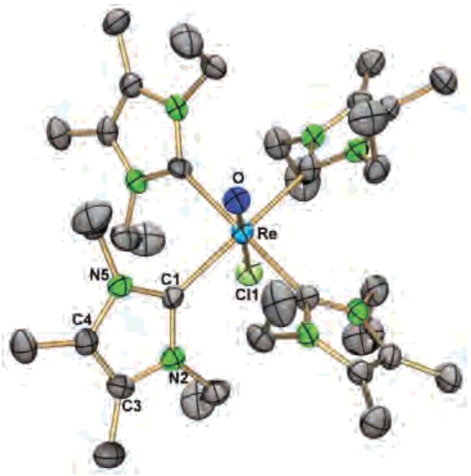

Figure 4. Ellipsoid representation[27] of the complex cation of $[ReOCl(L^{Et})_4]^{2+}$. Thermal ellipsoids represent 50% probability.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in the $[ReOCl(L^{Et})_4]^{2+}$ Cation

Re−O1	1.64(4)	Re−Cl1	2.28(1)
Re−C1	2.195(4)		
O1−Re−Cl	180	O1−Re−C1	89.5(3)
Cl1−Re−C1	90.5(3)		

The structure suggested by the NMR data and by comparison with the analogous complex with L^{Me} is confirmed by an X-ray diffraction study of the green crystals. They contain $[ReOCl(L^{Et})_4][PF_6]_2$ cocrystallized with 2 equiv of KPF_6. The O−Re−Cl axis is located along a 4-fold rotational axis, and the ligands are at a 43° angle to the ReC_4 plane. The molecular structure of the $[ReOCl(L^{Et})_4]^{2+}$ cation is shown in Figure 4; selected bond lengths and angles are summarized in Table 4. The rhenium−carbon bond lengths are unexceptional with respect to the values in the rhenium carbene complexes described vide supra and suggest that there are no significant differences between the complex types $[ReOCl(L^R)_4]^{2+}$, $[ReO(OMe)(L^R)_4]^{2+}$, and $[ReO_2(L^R)_4]^+$ or depending on the alkyl substitution of the N-heterocyclic carbenes. The Re═O bond of 1.65 Å is short, but in the expected range for a rhenium−mono-oxo bond.[26] It is, however, remarkable that the typical extension of O═Re−(equatorial)L angles[26] is not observed in $[ReOCl(L^{Et})_4]^{2+}$ or $[ReO(OMe)(L^{Me})_4]^{2+}$. This may be attributed to the steric repulsion of the bulky carbenes, which may also allow the

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(25) (a) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333. (b) Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B* **1978**, *34*, 923. (c) Johnson, J. W.; Brody, J. F.; Ansell, G. B.; Zentz, S. *Inorg. Chem.* **1984**, *23*, 2415. (d) Luck, R. L.; O'Neill, R. S. *Polyhedron* **2001**, *20*, 773. (e) Brewer, J. C.; Thorp, H. H.; Siagle, K. M.; Brudvig, G. W.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 3171.

(26) Bandoli, G.; Tisato, F.; Refosco, F.; Gerber, T. I. A. *Rev. Inorg. Chem.* **1999**, *19*, 187.

coordination of methoxo or chloro ligands in *trans* position of the oxo ligand.

When an excess of $L^{i\text{-}Pr}$ is reacted with $[ReOCl_3(PPh_3)_2]$ under ambient conditions, there is no evidence for the formation of the intermediate complex $[ReOCl(L^{i\text{-}Pr})_4]^{2+}$, and only the dioxo cation $[ReO_2(L^{i\text{-}Pr})_4]^+$ is recovered. Orange-red blocks of the cation as perrhenate salt can be recovered upon standing at room temperature. Addition of NH_4PF_6 yields $[ReO_2(L^{i\text{-}Pr})_4][PF_6]$ as orange-red blocks. These salts are stable indefinitely in solution and as solids and are resistant to ligand substitution by chelating ligands such as 1,2-bis(diphenylphosphino)ethane. As reported,[19] the Re═O vibration of the dioxo unit is found in the IR spectrum at 775 cm^{-1}, a typical value for dioxo rhenium moieties and close to the vibrational frequency for this unit in the analogous complex $[ReO_2(L^{Me})_4]^+$. Both the proton and carbon NMR spectra show split signals for the methyl groups of the isopropyl substituents (^1H $\delta = 1.215$ and 0.796 ppm, ^{13}C $\delta = 21.33$ and 20.39 ppm), indicating hindered rotation due to the considerable steric bulk of the ligand. The carbene carbon signal comes at 173.5 ppm. This chemical shift is nearly identical to that of $[ReO_2(L^{Me})_4]^+$ and slightly higher than for the mono-oxo complex $[ReO(OMe)(L^{Me})_4]^{2+}$.

The X-ray crystal structures of the salts show well separated anions and cations. The complex rhenium atom in the $[ReO_2(L^{i\text{-}Pr})_4]^+$ cation has a truncated octahedral coordination of rhenium, with the oxo ligands occupying the axial positions. An ellipsoid depiction of the complex cation is found in Figure S1 (Supporting Information). Selected bond lengths and angles are contained in Table 3. Both the Re−O and Re−C bond lengths (1.78 and 2.22 Å, respectively) are negligibly longer than those in the corresponding complex with L^{Me}, $[ReO_2(L^{Me})_4]^+$, making significant differences in the electronic properties of the ligands unlikely. The angles between the ReC_4 plane and the planes of the heterocycles (52.4(2)−57.5(2)°) are significantly larger than in the analogous complexes with the smaller ligands L^{Me} and L^{Et}, where the corresponding angles are closer to 45°. This difference is apparently an effect of the appreciable steric bulk of the isopropyl groups and indicates that the difference in steric hindrance between the isopropyl and ethyl substituents plays a decisive role in the structure of such N-heterocyclic carbene complexes, whereas the difference between the methyl and ethyl substituents is less important.

Conclusion

Air-stable rhenium(V) oxo complexes of the compositions $[ReOCl(L^R)_4]^{2+}$ or $[ReO_2(L^R)_4]^+$ are formed during reactions of $[ReOCl_3(PPh_2)_2]$ with 3,4-dimethyl-2,5-dialkyl substituted N-heterocyclic carbenes (L^R). The chloro ligand of the former compound can readily be exchanged by methoxo ligands during the reaction with methanol. The stability of the products is controlled by the alkyl substituents of the nitrogen atoms of the organometallic ligands. The rhenium−carbon bonds mainly possess σ character. The mono-oxo species are stable to atmospheric conditions for a limited amount of time; the dioxo species are stable indefinitely.

The new rhenium complexes are of remarkable stability, and despite their large steric bulk, the four equatorial carbene ligands are not subject to exchange reactions, whereas similar dioxo compounds with amine ligands such as $[ReO_2(pyridine)_4]^+$ are frequently used as precursors in ligand exchange procedures with the pyridines as outgoing ligands.[28]

Acknowledgment. We thank Hermann-Starck AG, Goslar, for providing us with rhenium metal.

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

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