Multiple Bonds between Main-Group Elements and Transition Metals, 140. Cycloaddition Reactions of Methyltrioxorhenium(VII): Diphenylketene and Sulfur Dioxide

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Multiple Bonds between Main-Group Elements and Transition Metals. 140.[1] Cycloaddition Reactions of Methyltrioxorhenium(VII): Diphenylketene and Sulfur Dioxide

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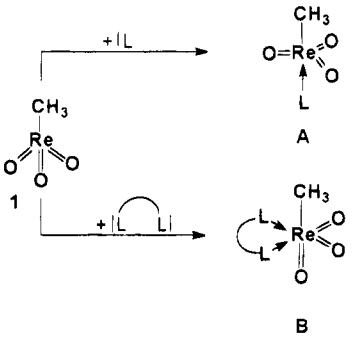
Complexation of methyltrioxorhenium(VII) (MTO; **1**) with mono- and bidentate nitrogen bases facilitates O,O′-cycloaddition reactions of this compound. bpy·CH_3ReO_3 (**2**; bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and py·CH_3ReO_3 (**3**; py = 4-*tert*-butylpyridine) thus react with the heterocumulenes diphenylketene and SO_2 in *regioselective* cycloadditions at the O=Re=O fragment, resulting in the new metallacyclic compounds (bpy)$CH_3Re(=O)[\eta^2$-$O_2C(=O)CPh_2]$ (**4a**), $(py)_2CH_3Re(=O)[\eta^2$-$O_2C(=O)CPh_2]$ (**6**) and (bpy)$CH_3Re(=O)(\eta^2$-$O_2SO_2)$ (**7**). Metallacycles of this type are independently accessible from (bpy)$CH_3Re(=O)Cl_2$ (**5**). A single-crystal X-ray diffraction study of **4a** documents the regioselectivity of cycloaddition (crystal data: space group $P\bar{1}$, a = 1195.1(3) pm, b = 1380.0(3) pm, c = 1391.3(2) pm, α = 67.00(2)°, β = 77.91(1)°, γ = 73.17(1)°, Z = 2).

Introduction

Cycloaddition/reversion chemistry of oxo complexes is a rapidly developing field of organometallic chemistry.[2] The organorhenium oxide $(\eta^5$-$C_5Me_5)ReO_3$ is known to undergo formal [3 + 2] or [3 + 1] cycloadditions to the O=Re=O fragment with heterocumulenes such as diphenylketene and sulfur dioxide.[3,4] Similar reactions are known for the peroxide complexes of group 8–10 metals L_2MO_2 (L = PPh_3, $AsPh_3$; M = Pt, Pd, Ir, Rh).[5] It was therefore at first sight surprising that the parent compound CH_3ReO_3 (**1**)[6] does not show any reactivity with these substrates, even under more drastic conditions. In view of the availability of "modified" CH_3ReO_3, such that base ligands L can add to the Lewis-acid metal to form complexes **A** and **B**[7] (Scheme 1), we investigated whether complexation of CH_3ReO_3 with pyridine bases results in a change of reactivity compared to the unligated compound. The results obtained with the type **B** adduct bpy·CH_3ReO_3 (**2**; bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and the type **A** adduct py·CH_3ReO_3 (**3**; py = 4-*tert*-butylpyridine) are published in the present paper.

Scheme 1



Results and Discussion

(1) Cycloaddition of Diphenylketene. Introduced into organometallic chemistry in the 1970s,[8] ketenes insert into metal–ligand bonds of organometallic compounds or π-coordinate to metals. Two coordination modes for transition-metal ketene complexes are known: the η^2(C=O) mode for early transition metals and the η^2(C=C) mode for late transition metals. X-ray structures are known for both cases,[9–12] with some of these complexes being related to model systems for the Fischer–Tropsch reaction.[13]

We now have found that diphenylketene reacts with complex **2** according to Scheme 2 to give the five-

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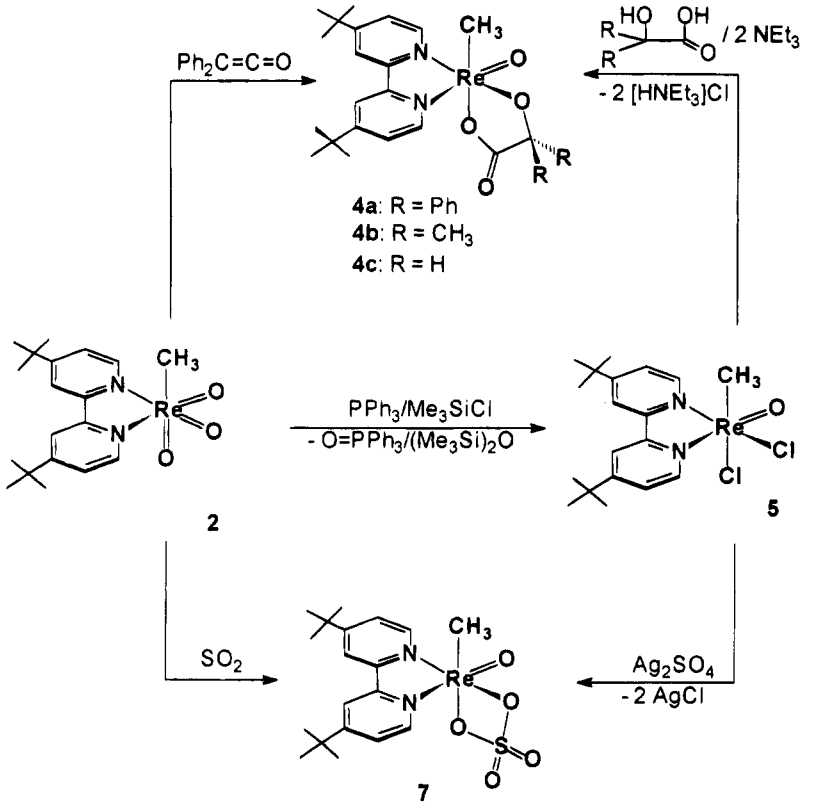
Scheme 2. (Ph = C_6H_5)



membered metallacycle (bpy)$CH_3Re(=O)[\eta^2$-$O_2C(=O)$-$CPh_2]$ (**4a**) as a violet powder. **4a** results from a net [3 + 2] cycloaddition of the ketene C=C bond across a O=Re=O unit of **2**. The C—C distance within the ReO_2C_2 five-membered ring (*envelope* conformation; Figure 1) falls in the normal range for single bonds. All bond distances and angles of the metallacyclic core structure are close to those of the related cycloadduct of $(\eta^5$-$C_5Me_5)ReO_3$ with diphenylketene.[3] Two Re—O bond distances are asymmetrically elongated (Re—O2 = 205.6(3) pm and Re—O3 = 194.1(3) pm) as a consequence of the formation of two different carbon—oxygen bonds (O2—C2(sp^2) = 131.1(5) pm and O3—C3(sp^3) = 143.5(5) pm). By way of contrast, the corresponding Re—O bond distances of the related glycolate complexes of $(\eta^5$-$C_5Me_5)ReO_3$[14] or (1,4,7-triazacyclononane)ReO_3[15] are nearly identical (196.5(2) pm, mean values). The Re—O1 and Re—C1 bond distances (168.4(3) and 213.3(5) pm, respectively) are typical of multiple and single bonds, respectively.

The planes defined by the atoms Re,N1,N2,C20,C25 and the ReO_2C_2 ring form an angle of about 79°. The coordination geometry of **4a** is thus best described as a (strongly) distorted octahedron. A nearly ideal octahedral coordination is seen in the pyridine base adducts of osmate esters where a *trans*-osmyl group, $[OsO_2]^{2+}$, is present.[16]

The ^{13}C NMR spectra exhibit signals at δ 184.21 ppm (CO) and δ 95.32 ppm (CPh_2) for the metallacyclic carbon atoms. A strong ν(C=O) band in the IR spectra at 1670 cm^{-1} is assigned to the carbonyl group. This is in close agreement with the X-ray structure data.

A similar type of reaction is found for the organometallic oxide $(\eta^5$-$C_5Me_5)ReO_3$.[3] The *isoelectronic* anion $[(\eta^5$-$C_5Me_5)WO_3]^-$, however, reacts with ketenes to give products resulting from net [2 + 2] cycloadditions of W=O across the ketene C=C bond.[17] Since **2** has a stereochemically rigid type **B** structure (as does 2,2′-bipyrimidine—CH_3ReO_3 (X-ray diffraction); see Scheme 1),[18] the three possible regioisomers **4**, **4′**, and **4″** as well as their enantiomers can be formed in the course of the addition of diphenylketene to **2** (Chart 1). ^1H and ^{13}C NMR data clearly show that only one isomer occurs, which was structurally characterized by X-ray diffraction. Each ring of the bipyridine ligand is different, as seen by a doubling of NMR signals. The signals of the ring located *trans* to Re=O are shifted more downfield than the signals of the other ring.

(2) Reductive Chlorination. Complex **2** is reduced by triphenylphosphine/trimethylchlorosilane to the known rhenium(V) compound (bpy)$CH_3Re(=O)Cl_2$ (**5**).[19] Both chlorine atoms are in *cis*-positions to each other.[20] One of the chlorine ligands is located in an equatorial and the other in an axial position with respect to the bipyridine ligand. If **5** is reacted with α-hydroxyacetic

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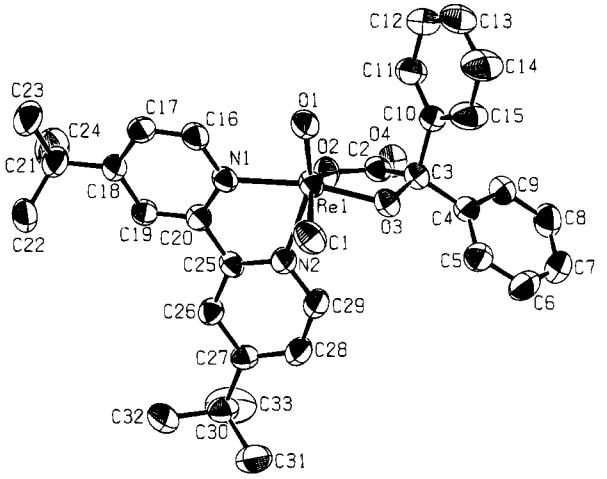
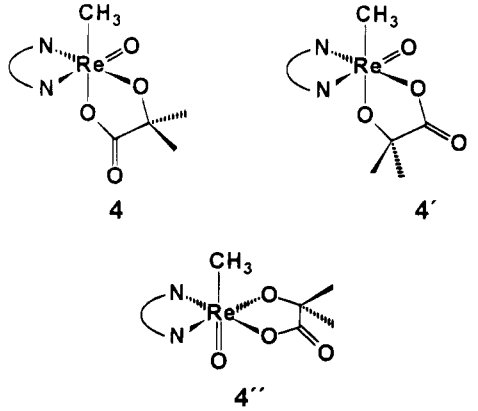


Figure 1. Crystal structure of the [3 + 2] cycloadduct **4a**, showing 50% probability ellipsoids and the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected distances (pm) and angles (deg): Re—O(1) = 168.4(3), Re—O(2) = 205.6(3), Re—O(3) = 194.1(3), Re—C(1) = 213.3(5), Re—N(1) = 215.0(3), Re—N(2) = 223.7(4), O(2)—C(2) = 131.1(5), C(2)—C(3) = 155.4(5), C(2)—O(4) = 120.0(5), C(3)—O(3) = 143.5(5); C(3)—C(4) = 151.4(5), C(3)—C(10) = 154.4(5); O(2)—Re—O(1) = 111.9(2), O(3)—Re—O(1) = 108.4(1), C(1)—Re—O(1) = 98.7(2), N(1)—Re—O(1) = 86.5(1), N(2)—Re—O(1) = 157.3(1), C(1)—Re—O(2) = 148.4(2), O(3)—Re—O(2) = 79.2(1), N(1)—Re—O(2) = 91.8(1), N(2)—Re—O(2) = 75.2(1), N(1)—Re—O(3) = 164.6(1), C(1)—Re—O(3) = 84.0(2), N(2)—Re—O(3) = 94.0(1), N(1)—Re—C(1) = 98.0(2), N(2)—Re—C(1) = 79.5(2), N(2)—Re—N(1) = 71.5(1), C(2)—O(2)—Re = 115.7(2), C(3)—C(2)—O(2) = 113.4(3), C(2)—C(3)—O(3) = 107.4(3), C(3)—O(3)—Re = 114.4(2).

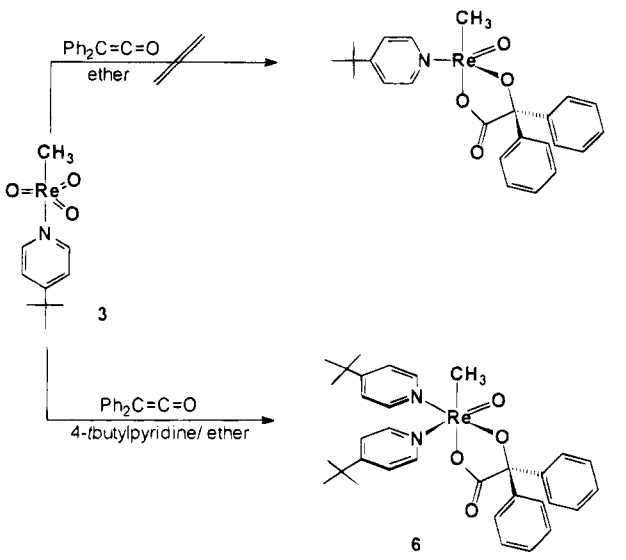
Chart 1



acids and triethylamine, (bpy)$CH_3Re(=O)[\eta^2$-$O_2C(=O)CPh_2]$ species (**4a**, R = Ph; **4b**, R = CH_3, **4c**, R = H) are obtained (see Scheme 2). A single isomer is once again formed, as shown by ^1H and ^{13}C NMR data. Even with small substituents R (e.g., R = H) the reaction **5** → **4** is regioselective, suggesting that the size of R does not have a great deal of influence upon the regioselectivity.

(3) Penta- *vs* Hexacoordination. The precise composition of the starting complex—pentacoordinate **A** *vs* hexacoordinate **B**—proved important for the above-mentioned cycloaddition. For example, the monoadducts **3** do not react with the ketene in a defined way. In contrast, instantaneous cycloaddition occurred in the presence of excess pyridine base (Scheme 3), yielding the complex $(py)_2CH_3Re(=O)[\eta^2$-$O_2C(=O)CPh_2]$ (**6**) in

Scheme 3



84% yield. Note that compound **3** does not react with *tert*-butylpyridine to give the (unknown) adduct CH_3ReO_3·2py even if the base concentration is 10 times higher than the concentration of **3** (*in situ* ^{17}O NMR spectroscopy). It is known that the addition of a base to R—ReO_3 compounds in general will shift the oxygen resonance significantly.[21] In contrast, the addition of *tert*-butylpyridine to a solution of **3** has no influence upon the ^{17}O chemical shift. The situation for **3** is comparable to the chemistry of OsO_4, which forms adducts of composition OsO_4·L with pyridine bases (L). The cycloaddition products formed by reaction of olefins with OsO_4 normally contain two pyridine ligands.[22]

(4) Cycloadditions of Sulfur Dioxide. Metal complexes of sulfur dioxide were first reported as early as 1938.[23] Several coordination modes of SO_2 *via* S, O, or S=O are now known.[24] **2** reacts with SO_2 according to Scheme 2 to give the four-membered metallacycle (bpy)$CH_3Re(=O)(\eta^2$-$O_2SO_2)$ (**7**). The reaction is a net [3 + 1] cycloaddition of the sulfur atom across the O=Re=O unit of **2**, with concomitant oxidation of the sulfur atom (formally $S^{4+} \rightarrow S^{6+}$). This complex is best described as a sulfonato-*O*,*O*′ complex. A similar reaction is known for $(\eta^5$-$C_5Me_5)ReO_3$,[4] but *not* for CH_3ReO_3. The cycloaddition of SO_2 to **2** is regioselective, as unequivocally shown by the ^1H NMR (Figure 2) and ^{13}C NMR spectra. The structure of **7** is also supported by an alternative synthesis: treatment of the dichloro Re(V) precursor compound **5** with silver sulfate in methylene chloride (Scheme 2). It should be noted that sulfur dioxide does *not* react with type **A** complexes even when an excess of 4-*tert*-butylpyridine was employed (see above).

(5) Thermogravimetry/Mass Spectrometry. The question regarding the cycloreversion was checked by TG/MS studies. Two peaks were observed between 150 and 260 °C for **6**. These are located very close to one

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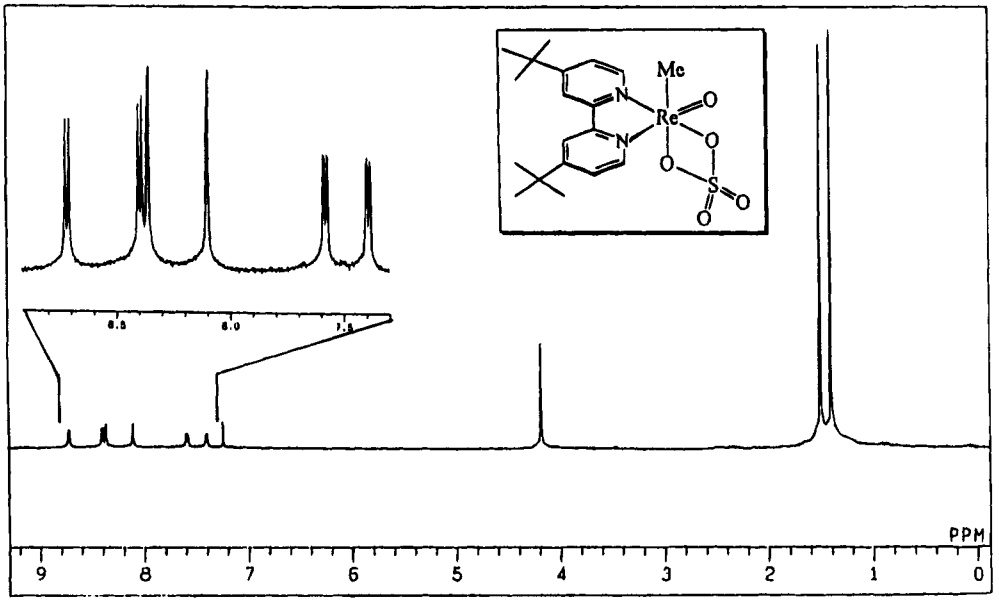

Figure 2. ^{1}H NMR spectra of the sulfur dioxide cycloadduct **7**. The signals belonging to the bipyridine ring in a position *trans* to Re=O are shifted more downfield than the signals of the other ring.

another (Figure 3). The predominant decomposition products are 4-*tert*-butylpyridine at 150 °C and benzophenone at 260 °C. Methane is observed above ca. 190 °C. Carbon dioxide is extruded with concomitant formation of benzophenone. Finally, carbon dioxide and water are formed at 450 °C by an internal combustion of the compound. The TG onset is ill-defined (80–90 °C). The weight of the residue suggests ReO_2 as the final product. Compound **4a** exhibits a similar decomposition (Figure 4). At the extrapolated onset of 248 °C carbon dioxide, methane, benzophenone and 4,4′-di-*tert*-butyl-2,2′-bipyridine are formed. Benzophenone can be detected even at lower temperatures (~150 °C). Again, the weight of the residue suggests ReO_2 as the final product. The products of decomposition are reminiscent of RuO_4 chemistry.[25]

The η^2-sulfato-*O,O′* complex **7** shows a different mode of decomposition (Figure 5): sulfur dioxide, methane, and 4,4′-di-*tert*-butyl-2,2′-bipyridine are formed above the onset temperature at 230 °C. All products of this decomposition process are volatile. (Re_2O_7 is known to be volatile under these conditions.) Therefore, the total weight of the residue is less than 5%. SO_2 forms thermally from the cycloadduct of this molecule in a cycloreversion type of reaction.

Conclusion

Chemical reactions of nitrogen base adducts of CH_3ReO_3 occur in the oxo ligand periphery. Addition of heterocumulenes such as diphenylketene and sulfur dioxide *via* cycloaddition leads to Re(V) metallacycles with *O,O′* ligands. These metallacycles do not form from CH_3ReO_3 in the absence of base ligands. Similar to the osmylation reaction, one of the effects of added ligand is to stabilize the coordinatively unsaturated metallacycles.[26,27] A result of this observation is that the nitrogen base adducts of CH_3ReO_3 are chemically more related to $(\eta^5\text{-}C_5Me_5)ReO_3$ than to CH_3ReO_3. The excellent regioselectivity of the cycloadditions does not simply originate from the steric demands of the adducts. Our observation of altered reactivity of the organometallic oxide CH_3ReO_3 upon addition of base ligands is in line with the chemistry of OsO_4: it was just recently shown that the normally unreactive fluorinated olefins add instantaneously to OsO_4 when pyridine is present.[16] A reasonable explanation is that *polar* MO_2 (M = Os, Re) core structures form from CH_3ReO_3 and OsO_4 upon coordination of base (hexacoordination). These can attack C–C multiple bonds in the described way.[27] Work is underway to activate CH_3ReO_3 for reactions with olefins.

Experimental Section

All experiments were carried out under a nitrogen atmosphere using Schlenk techniques. The starting compounds **1**,[6] **2**,[7] **5**,[19] and diphenylketene[28] were prepared according to published methods. Triphenylphosphine was recrystallized from *n*-hexane before use. The other chemicals were used as purchased. ^{1}H NMR (400 MHz) spectra were recorded on a JEOL JNM GX-400; mass spectra were recorded at 70 eV on a Finnigan MAT 311-A. Elemental analyses were performed in the microanalytical laboratory of our institute (M. Barth). Mass spectra (*m/z* values) are based on the ^{187}Re isotope. TG/MS measurements were performed with a TGA 7 thermobalance (Perkin-Elmer) and a QMG 420 mass spectrometer (Balzers) coupled through a capillary system heated to 280 °C. The measurements were preformed under a dynamic He atmosphere (45 sccm) at a pressure of 1 atm. The samples (1.5–5 mg) were heated at a rate of 10 K/min in the range 50–700 °C.

(1) (4-*tert*-Butylpyridine)methyltrioxorhenium (3). 4-*tert*-Butylpyridine (195 μL, 2.0 mmol) was added to a solution of **1** (250 mg, 1.0 mmol) in 10 mL of diethyl ether. The solution turned yellow. The mixture was stirred for 2 h and then

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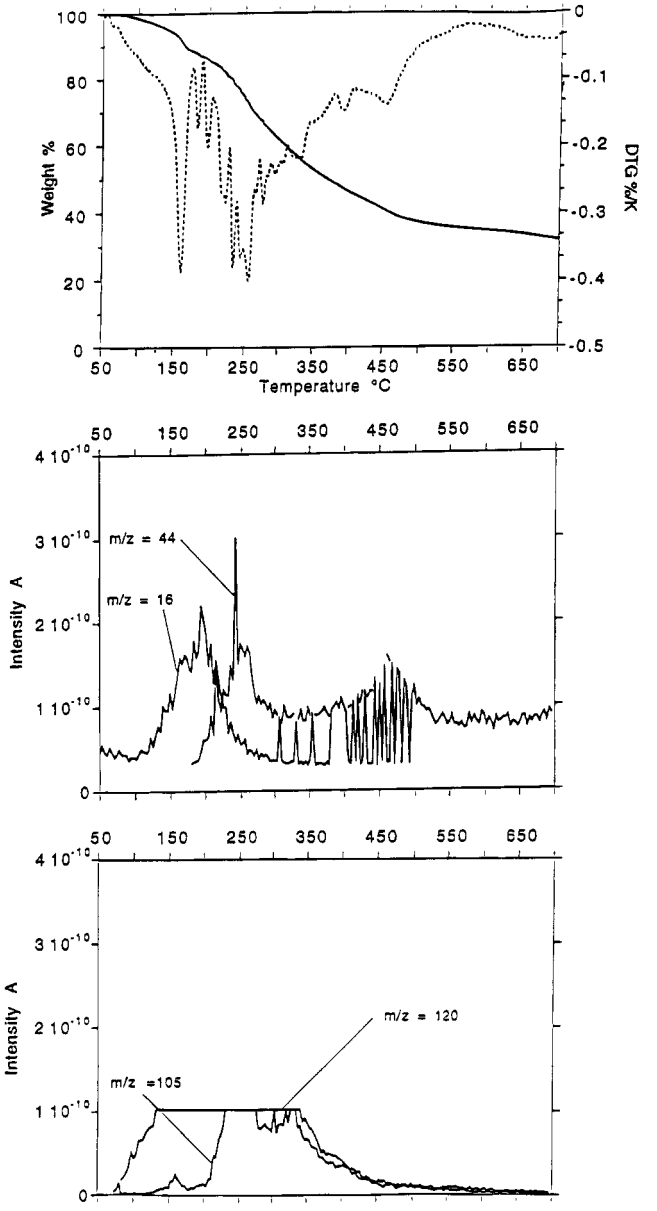

Figure 3. TG curve, DTG curve, and MS intensities of **6**. The following products are noted: methane (*m*/*z* 16); carbon dioxide (*m*/*z* 44); benzophenone (*m*/*z* 105); *tert*-butylpyridine (*m*/*z* 120).

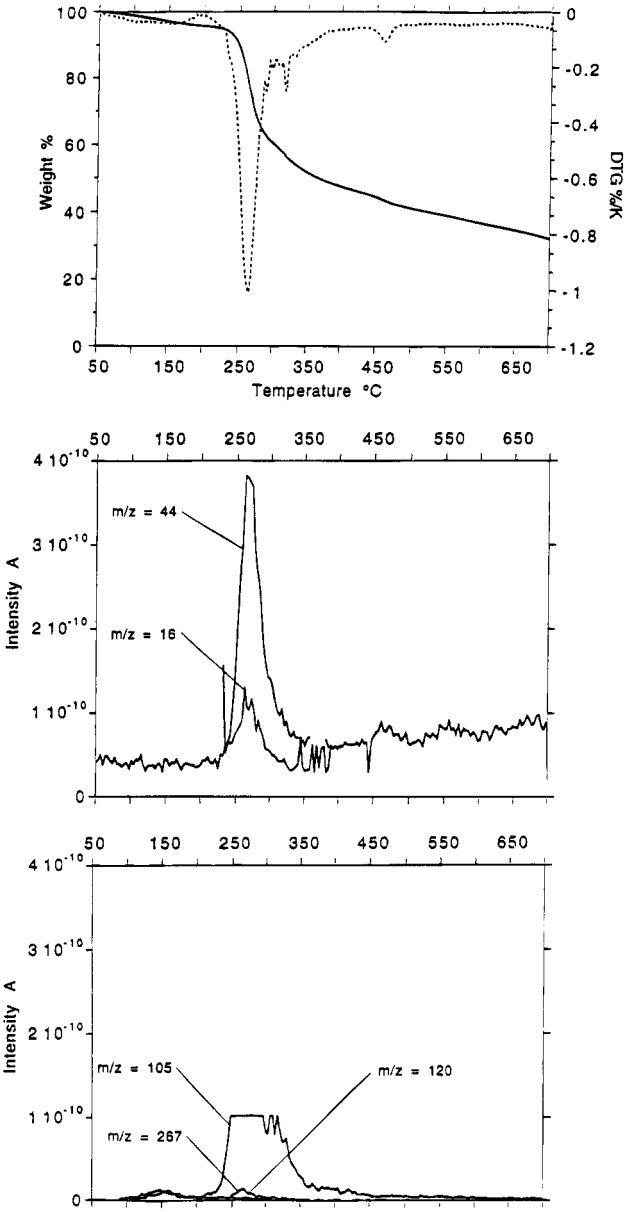

Figure 4. TG curve, DTG curve, and MS intensities of **4a**. The following products are noted: methane (*m*/*z* 16); carbon dioxide (*m*/*z* 44); benzophenone (*m*/*z* 105), *tert*-butylpyridine (*m*/*z* 120); 4,4′-di-*tert*-butyl-2,2′-bipyridine (*m*/*z* 267).

concentrated to ca. 5 mL. A yellow precipitate was obtained upon cooling to −78 °C, which was washed with pentane and dried in vacuo. Yield: 200 mg (52%). Anal. Found (calcd) for $C_{10}H_{16}O_3NRe$ (M_r 384.45): C, 31.43 (31.24); H, 4.19 (4.19); N, 3.60 (3.64); Re, 48.47 (48.43).

Spectroscopic data: IR (KBr; ν, cm^{-1}) 2965 m (ν(C—H)), 1613 m (ν(C=C)), 1420 m, 929 vs (ν(Re=O)); ^1H NMR (400 MHz, $CDCl_3$, 30 °C; δ, ppm) 1.26 ($(CH_3)_3C$, s, 9H), 1.80 ($ReCH_3$, s, 3H), 7.34 (N(CH)(C*H*), dd, $^3J(H,H) = 4.88$, $^4J(H,H) = 1.83$ Hz, 2H), 8.13 (N(CH), dd, $^3J(H,H) = 4.88$, $^4J(H,H) = 1.83$ Hz, 2H); $^{13}C\{^1H\}$ NMR (100.51 MHz, $CDCl_3$, 30 °C; δ, ppm) 25.15 ($ReCH_3$), 30.17 ($(CH_3)_3C$), 35.00 ($(CH_3)_3C$), 122.17 (N(CH)-(CH)$_2$), 146.44 (N(CH)(CH)$_2$*C*), 163.62 (N(CH)); ^{17}O NMR (54.2 MHz, $CDCl_3$, room temp; δ, ppm) 881.92 (ReO_3); CI MS (70 eV; *m*/*z*) 271 ($[(NC_5H_4(C(CH_3)_3))_2]^+$, rel intens 14%), 136 ($[NC_5H_4(C(CH_3)_3)]^+$, 100%).

(2) (4,4′-Di-*tert*-butyl-2,2′-bipyridine)(2-hydroxy-2,2-diphenylacetato(2−)-*O*,*O*′)methyloxo rhenium (4a). (a) Diphenylketene (105 μL, 0.6 mmol) was added to a stirred suspension of **2** (260 mg, 0.5 mmol) in 10 mL of THF at room temperature. During the reaction the yellow suspension turned to a clear violet solution after 5 min. The solution was evaporated to dryness in vacuo after 30 min. The residue was washed with pentane and then dried in vacuo. Yield: 290 mg (74%). Anal. Found (calcd) for $C_{33}H_{37}N_2O_4Re$ (M_r = 711.87) + 1 equiv of THF: C, 56.73 (56.69); H, 5.60 (5.79); N, 3.70 (3.57); Re, 25.09 (23.75).

(b) Triethylamine (108 μL, 0.78 mmol) and benzilic acid (82 mg, 0.36 mmol) were added at room temperature to a stirred suspension of **5** (200 mg, 0.36 mmol) in 10 mL of toluene. The mixture was then refluxed for 60 min. After it was cooled to room temperature, the solution was filtered and evaporated in vacuo. The violet residue was washed with pentane and then dried in vacuo.

Spectroscopic data: IR (KBr; ν, cm^{-1}) 2963 m, 2872 m, 1670 vs (ν(C=O)), 1617 vs, 1543 w, 1489 s, 993 m, 978 vs; ^1H NMR (400 MHz, $CDCl_3$, 25 °C; δ, ppm) 1.30 ($(CH_3)_3C$, s, 9H), 1.44 ($(CH_3)_3C'$, s, 9H), 3.74 ($ReCH_3$, s, 3H), 6.73 (bpy H-5, dd, $^3J(H,H) = 6.10$, $^4J(H,H) = 1.83$ Hz, 1H), 7.28−7.91 (phenyl + bpy, m, 23H), 8.22 (bpy H-3, d, $^4J(H,H) = 1.83$ Hz, 1H), 8.95 (bpy H-6′, d, $^3J(H,H) = 6.10$ Hz, 1H); $^{13}C\{^1H\}$ NMR (100.51

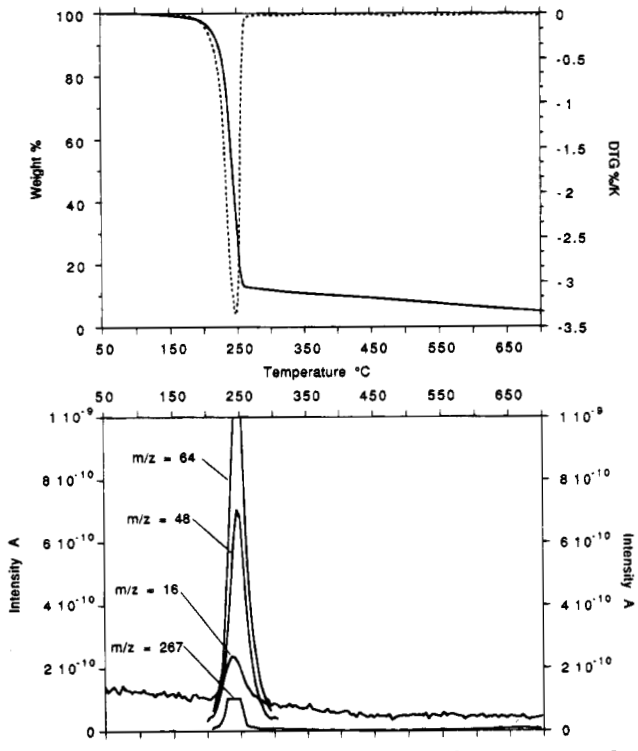

Figure 5. TG curve, DTG curve, and MS intensities of **7**. The following products are noted: methane (m/z 16); sulfur dioxide (m/z 48.64); 4,4′-di-*tert*-butyl-2,2′-bipyridine (m/z 267).

MHz, $CDCl_3$, 30 °C; δ, ppm) 2.91 ($ReCH_3$), 30.23 ($(CH_3)_3C$), 31.19 ($(CH_3)_3C'$), 34.14 ($(CH_3)_3C$), 35.12 ($(CH_3)_3C'$), 95.33 (Ph_2C), 117.12 (bpy C-5), 118.20 (bpy C-5′), 120.84 (bpy C-3), 122.25 (bpy, C-3′), 126.43, 126.87, 127.06, 127.70, 127.81, 127.84, 144.73, 145.46, 148.08, 148.41, 148.83, 152.63, 163.20 (bpy C-2), 165.41 (bpy C-2′), 184.21 (C=O); CI MS (70 eV; m/z) 712 ($[M]^+$, rel intens 78%), 444 ($[M]^+$ − bpy, 9%), 249 ($[CH_3ReO_3]^+$, 5%), 234 ($[ReO_3]^+$, 100%).

(3) (4,4′-Di-*tert*-butyl-2,2′-bipyridine)(2-hydroxy-2-methylpropionato(2−)-*O,O′*)methyloxorhenium (4b). Triethylamine (108 μL, 0.78 mmol) and 2-hydroxyisobutyric acid (44 mg, 0.42 mmol) were added at room temperature to a stirred suspension of **5** (210 mg, 0.38 mmol) in 10 mL of toluene. The mixture was then refluxed for 60 min. After it was cooled to room temperature, the solution was filtered and then evaporated in vacuo. The violet residue was washed with pentane and then dried in vacuo. Yield: 298 mg (96%). Anal. Found (calcd) for $C_{23}H_{33}N_2O_4Re$ (M_r 587.32) + 1/3 equiv toluene: C, 49.38 (49.20); H, 5.73 (5.81); N, 4.25 (4.53); Re, 28.12 (30.11).

Spectroscopic data: IR (KBr; ν, cm^{-1}) 2966 m, 2871 m, 1678 vs (ν(C=O)), 1618 s, 1414 m, 1193 s, 979 s, 965 m; ^1H NMR (400 MHz, $CDCl_3$, room temp; δ, ppm) 1.34 ($(CH_3)_3C$, s, 9H), 1.44 ($(CH_3)_3C'$, s, 9H), 1.60 ($(CH_3)_2C$—O, s, 3H), 1.81 ($(CH_3)'_2$C—O, s, 3H), 3.68 ($ReCH_3$, s, 3H), 7.14 (bpy H-5, dd, $^3J(H,H)$ = 5.50, $^4J(H,H)$ = 1.22 Hz, 1H), 7.47 (bpy H-5′, dd, $^3J(H,H)$ = 6.10, $^4J(H,H)$ = 1.83 Hz, 1H), 7.94 (bpy H-3, d, 1H), 8.21−8.22 (bpy H-3′ + H6, m, 2H), 8.95 (bpy H-6′, d, $^3J(H,H)$ = 6.71 Hz, 1H); $^{13}C\{^1H\}$ NMR (100.51 MHz, $CDCl_3$, room temp; δ, ppm) 1.37 ($ReCH_3$), 27.93 ($(CH_3)_2C$—O), 28.53 ($(CH_3)'_2C$—O), 30.33 ($(CH_3)_3C$), 31.24 ($(CH_3)_3C'$), 34.20 ($(CH_3)_3C$), 35.29 ($(CH_3)_3C'$), 89.40 (Ph_2C), 117.19 (bpy C-5), 118.47 (bpy C-5′), 120.90 (bpy C-3), 122.54 (bpy, C-3′), 147.58 (bpy C-4), 148.69 (bpy C-6), 149.00 (bpy C-6′), 152.59 (bpy C-4′), 163.50 (bpy C-2), 165.41 (bpy C-2′), 188.27 (C=O); CI MS (70 eV; m/z) 588 ($[M]^+$, rel intens 100%), 319 ($[M - bpy]^+$, 8%).

(4) (4,4′-Di-*tert*-butyl-2,2′-bipyridine)(2-hydroxyacetato-(2−)-*O,O′*)methyloxorhenium (4c). Triethylamine (108 μL, 0.78 mmol) and glycolic acid (32 mg, 0.42 mmol) were added at room temperature to a stirred suspension of **5** (210 mg, 0.38 mmol) in 10 mL of toluene. The mixture was then refluxed for 60 min. After this mixture was cooled to room temperature, the violet precipitate was filtered off. The remaining NEt_3·HCl was sublimed in vacuo at 120 °C thereafter. The residue was recrystallized from methylene chloride/hexane. Yield: 201 mg (90%). Anal. Found (calcd) for $C_{21}H_{29}N_2O_4Re$ (M_r 559.67) + 1/3 equiv of methylene chloride: C, 43.55 (43.57); H, 5.16 (5.08); N, 4.80 (4.76); O, 11.32 (10.88); Re, 32.58 (31.67).

Spectroscopic data: IR (KBr; ν, cm^{-1}) 2961 m, 1687 vs (ν(C=O)), 1618 vs, 1414 m, 1266 m, 974 m (ν(Re=O)); ^1H NMR (400 MHz, $CDCl_3$, room temp; δ, ppm) 1.35 ($(CH_3)_3C$, s, 9H), 1.44 ($(CH_3)_3C'$, s, 9H), 3.69 ($ReCH_3$, s, 3H), 5.27 (H_2C—O, d, $^2J(H,H)$ = 17.09 Hz, 1H), 5.50 (H_2C—O, d, $^2J(H,H)$ = 17.09 Hz, 1H), 7.18 (bpy H-5, dd, $^3J(H,H)$ = 6.10, $^4J(H,H)$ = 1.22 Hz, 1H), 7.48 (bpy H-5′, dd, $^3J(H,H)$ = 6.10, $^4J(H,H)$ = 1.83 Hz, 1H), 7.94 (bpy H-3, d, $^4J(H,H)$ = 1.22 Hz, 1H), 8.08 (bpy H-6, dd, $^3J(H,H)$ = 6.10 Hz, 1H), 8.23 (bpy H-3′, d, $^4J(H,H)$ = 1.22 Hz, 1H), 8.94 (bpy H-6′, dd, $^3J(H,H)$ = 6.71 Hz, 1H); $^{13}C\{^1H\}$ NMR (100.51 MHz, $CDCl_3$, room temp; δ, ppm) 2.10 ($ReCH_3$), 30.31 ($(CH_3)_3C$), 31.25 ($(CH_3)_3C'$), 34.22 ($(CH_3)_3C$), 35.34 ($(CH_3)_3C'$), 81.06 (Ph_2C), 117.23 (bpy C-5), 118.50 (bpy C-5′), 121.08 (bpy C-3), 123.10 (bpy C-3′), 147.01 (bpy C-4), 148.50 (bpy C-6), 149.12 (bpy C-6′), 152.68 (bpy C-4′), 163.75 (bpy C-2), 165.70 (bpy C-2′), 185.91 (C=O); CI MS (70 eV; m/z) 561 ($[M]^+$, rel intens 29%), 269 ($[bpy]^+$, 100%).

(5) Bis(4-*tert*-butylpyridine)(2-hydroxy-2,2-diphenylacetato(2−)-*O,O′*)methyloxorhenium (6). 4-*tert*-Butylpyridine (295 μL, 2.0 mmol) and diphenylketene (194 μL, 1.1 mmol) were added at room temperature to a stirred suspension of **1** (250 mg, 1.0 mmol) in 10 mL of diethyl ether. The solvent was decanted after 2 h; the solid was washed with pentane and then dried in vacuo. Yield: 600 mg (84%). Anal. Found (calcd) for $C_{33}H_{39}N_2O_4Re$ (M_r 713.95): C, 55.32 (55.52); H, 5.64 (5.51); N, 3.66 (3.92); Re, 25.73 (26.08).

Spectroscopic data: IR (KBr; ν, cm^{-1}) 2963 m, 1658 vs (ν(C=O)), 1619 vs, 1497 s, 1446 m, 959 vs (ν(Re=O)); ^1H NMR (400 MHz, $CDCl_3$, 25 °C; δ, ppm) 1.60 ($(CH_3)_3C$, s, 9H), 5.16 ($ReCH_3$, s, 3H), 7.20−7.23 (phenyl, m, 15H), 7.58 (py H-3, dd, $^3J(H,H)$ = 5.37, $^4J(H,H)$ = 1.47 Hz, 4H), 8.79 (py H-2, dd, $^3J(H,H)$ = 5.37, $^4J(H,H)$ = 1.47 Hz, 4H); $^{13}C\{^1H\}$ NMR (100.51 MHz, $CDCl_3$, 30 °C; δ, ppm) 7.64 ($ReCH_3$), 30.59 ($(CH_3)_3C$), 34.78 ($(CH_3)_3C$), 95.81 (Ph_2C), 121.71 (py C-3), 126.35, 126.78, 127.20, 144.15, 153.20, 165.32, 176.43 (C=O); FAB MS (70 eV; m/z) 715 ($[M]^+ + H^+$, rel intens 48%), 602 ($[M]^+ - 2$ *tert*-butyl, 14%), 369 (55%).

(6) (4,4′-Di-*tert*-butyl-2,2′-bipyridine)(sulfonato(2−)-*O,O′*)methyloxorhenium (7). (a) SO_2 was bubbled (ca. 1 bubble/s) at room temperature for 2 h into a stirred suspension of **2** (260 mg, 0.5 mmol) in 10 mL of THF. During the reaction the yellow suspension warmed up and turned into a clear brown solution. A green microcrystalline green solid precipitated after ca. 10 min. After the solvent was decanted, the solid was washed with pentane and then dried in vacuo. Yield: 291 mg (99%). Anal. Found (calcd) for $C_{19}H_{27}N_2O_5ReS$ (581.70): C, 38.95 (39.23); H, 4.86 (4.68); N, 5.19 (4.82); S, 5.50 (5.51); Re, 31.71 (32.02).

(b) Ag_2SO_4 (312 mg, 1.0 mmol) was added to a stirred suspension of **5** (210 mg, 0.38 mmol) in 10 mL of methylene chloride, and the mixture was stirred for 2 days in the dark at room temperature. The solution was filtered and then evaporated in vacuo. The green residue was washed with pentane and then dried in vacuo.

Spectroscopic data: IR (KBr; ν, cm^{-1}) 1316 s, 1174 vs (ν(S=O)), 1123 m, 998 vs ν(Re=O)), 888 m, 856 m, 674 vs (ν(S=O)); ^1H NMR (400 MHz, $CDCl_3$, 30 °C; δ, ppm) 1.40 ($(CH_3)_3C$, s, 9H), 1.50 ($(CH_3)_3C'$, s, 9H), 4.18 ($ReCH_3$, s, 3H), 7.39 (bpy H-5, dd, $^3J(H,H)$ = 6.71, $^4J(H,H)$ = 1.83 Hz, 1H), 7.58 (bpy H-5′, dd, $^3J(H,H)$ = 6.72, $^4J(H,H)$ = 1.83 Hz, 1H), 8.10 (bpy H-3, d, $^4J(H,H)$ = 1.22 Hz, 1H), 8.36 (bpy H-3′, d, $^4J(H,H)$ = 1.84 Hz, 1H), 8.39 (bpy H-6, d, $^3J(H,H)$ = 6.10, 1H), 8.72 (bpy H-6′, d, $^3J(H,H)$ = 6.11 Hz, 1H); $^{13}C\{^1H\}$ NMR

(100.51 MHz, $CDCl_3$, 30 °C; δ, ppm) 5.02 ($ReCH_3$), 30.36 ($(CH_3)_3C$), 31.17 ($(CH_3)_3C'$), 34.70 ($(CH_3)_3C$), 35.56 ($(CH_3)_3C'$), 118.28 (bpy C-5), 118.69 (bpy C-5′), 122.05 (bpy C-3), 123.59 (bpy, C-3′), 148.27 (bpy C-4), 148.50 (bpy C-6), 149.90 (bpy C-6′), 152.76 (bpy C-4′), 164.96 (bpy C-2), 167.50 (bpy C-2′); CI MS (70 eV; *m/z*) 269 (bpy^+, rel intens 30%), 153 (100%).

(7) Crystal Structure Determination. **4a** crystallizes from a toluene solution at 20 °C as red prisms: a = 1195.1(3) pm, b = 1380.0(3) pm, c = 1391.3(2) pm; α = 67.00(2)°, β = 77.91(1)°, γ = 73.17(1)°; $V = 2009 \times 10^6$ pm^3; measurement at 23 °C; ϱ_{calc} = 1.296 g cm^{-3}; μ = 31 cm^{-1}; F_{000} = 792; Z = 2; triclinic crystal system; space group $P\bar{1}$ (No. 2); Enraf-Nonius CAD4; λ = 71.07 pm (Mo Kα, graphite monochromator); range of measurement 1.0° < Θ <25°; ω scan; scan width (0.8 + 0.35·tan Θ)° (±25% before and after each reflection to determine the background); t_{max} = 60 s; 7349 measured reflections ($\pm h,k,\pm l$); 6681 independent reflections, 6125 of which had $I > 3\sigma(I)$; structure determination with Patterson methods and difference Fourier synthesis; empirical absorption correction based on Ψ-scan data; transmission coefficients 0.708–1.0; 554 least-squares parameters; all 45 heavy atoms with anisotropic thermal parameters; all 8 hydrogen atoms of the THF solvent calculated; all other hydrogen atoms found and independently refined (isotropic); anomalous dispersions[29] accounted for; shift/error <0.002; $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.039$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.040$; residual electron density +2.22/−0.63 e/Å^3; weighting scheme of Tukey and Prince[30] with three refined parameters $P(1) = 1.905$, $P(2) = 0.823$, $P(3) = 1.487$. All calculations were performed on a DECstation 5000/25 using the programs CRYSTALS[31] and PLATON.[32] For further details of the crystal structure determination, the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, may be contacted; please quote the reference to this paper, the names of the authors, and the registration number CSD-58620.

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Supplementary Material Available: Tables of positional and thermal parameters and all bond distances and angles for **4a** (9 pages). Ordering information is given on any current masthead page.

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