Complex **8** did not react, even under rather drastic conditions, with *p*-TCD, and we found that **8** cannot be considered as a source of **1**. Its synthesis, structure, and chemical behavior will be reported in a forthcoming paper.[34]

Conclusions

Complex **1** exemplifies the two main characteristics that have to be considered in studying the interaction of CO_2 with transition-metal complexes, namely the presence of acidic–basic sites in the structure and the possibility for the metal to transfer either one or two electrons. The assistance of the polydentate ligand is not only that of providing the correct electronic balance at the metal and having oxygen donor atoms for binding a second reactive site. In addition, it can provide reactive sites on which the reaction can actually occur. All these aspects have been emphasized by the results obtained in the reaction of the bifunctional complex **1** with different CO_2-like molecules, which maintain at least one of the main features of carbon dioxide.

Registry No. **1**, 71369-90-9; **4**, 67530-50-1; **6**, 104265-15-8; **8**, 104114-53-6; Co(salen), 14167-18-1; RNCO (R = 1-naphthyl), 86-84-0; PhNCO, 103-71-9; H_2salen, 94-93-9; DEKM, 609-09-6; methyl pyruvate, 600-22-6; dimethyl dimethyltartrate, 74956-34-6; 1,3-bis(1-naphthyl)urea, 607-56-7; 1,3-diphenylurea, 102-07-8; *p*-tolylcarbodiimide, 726-42-1; tetra-*p*-tolyloxalamidine, 75390-40-8; diphenylketene, 525-06-4.

Supplementary Material Available: Isotropic and anisotropic thermal parameters (Tables SI and SII) and equations of least-squares planes (Table SIII) for complex **8** (4 pages); tables of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
Clemson University, Clemson, South Carolina 29634-1905

Use of Bromine(I) Fluorosulfate for the Preparation of New *N*-Bromo Sulfonimides

Sukhjinder Singh and Darryl D. DesMarteau*

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Bromine(I) fluorosulfate has been known for more than 2 decades.[1] The compound is a potent oxidizer with the bromine atom being one of the most electrophilic halogens available in a neutral compound. The high thermal stability of $BrOSO_2F$ (up to 150 °C) is rather unexpected in view of the low stability of BrCl and $BrONO_2$.[2] Addition reactions with olefins occur readily,[3,4] and a large number of covalent chlorides[5–7] are found to react with $BrOSO_2F$ in the following way:

$$MCl_n + nBrOSO_2F \rightarrow M(OSO_2F)_n + nBrCl$$

Direct reaction of $BrOSO_2F$ with metals has proved very useful for the preparation of fluorosulfates of the 4d and 5d transition series.[8–10]

With appropriate electron-withdrawing groups on nitrogen, *N*-halogen derivatives can approach the reactivity of some *O*-halogen compounds for chlorine and bromine as illustrated by the compounds $(CF_3SO_2)_2NCl$[11,12] and $(FSO_2)_2NCl$.[13] In the course of research with $(CF_3SO_2)_2NCl$,[12] we became increasingly interested in preparing the *N*-bromo analogue. It was obvious that the N–Br bond would be highly reactive and the compound would represent an extremely useful synthon. However, all attempts to prepare it by methods analogous to the preparation of $(CF_3SO_2)_2NCl$ failed. The reaction of Cl_2 on $(CF_3SO_2)_2NAg$ or $[(CF_3SO_2)_2N]_2Hg$ had produced the *N*-chloro derivative in very high yield.[12] However, Br_2 failed to react with either the silver(I) or mercury(II) derivatives. Reaction of Br_2 with $AgN(SO_2CF_3)_2$ in diethyl ether resulted in the immediate precipitation of AgBr but no *N*-bromo derivative could be isolated. Use of other solvents failed to provide a route to $(CF_3SO_2)_2NBr$.

Halogen fluorosulfates have been used effectively to generate other *O*-halogen derivatives by metathesis reactions with oxo salts, e.g.[14]

$$XOSO_2F + CsOClO_3 \rightarrow XOClO_3 + CsSO_3F$$
$$X = Cl, Br$$

To our knowledge, related reactions with imides had not been attempted, and we speculated that $BrOSO_2F$ might be an effective route to the desired *N*-bromo compound by reaction with $AgN(SO_2CF_3)_2$. This reaction was indeed successful but was complicated by side reactions.

$$AgN(SO_2CF_3)_2 \xrightarrow[22\ ^\circ C]{BrOSO_2F} \underset{42\%}{(CF_3SO_2)_2NBr} + AgSO_3F + Ag_3(SO_3F)_4 + Br_2$$

The $AgSO_3F$ formed initially was further oxidized by $BrOSO_2F$ under the reaction conditions,[10] and the Br_2 formed was difficult to remove from the desired product. The use of alkali-metal salts was not attempted because of the possible complications due to complex formation between $BrOSO_2F$ and MSO_3F.[15,16] However, the reaction between $Hg[N(SO_2CF_3)_2]_2$ and $BrOSO_2F$ yielded the desired product in a very clean fashion according to

$$Hg[N(SO_2CF_3)_2]_2 + 2BrOSO_2F \xrightarrow[\sim 12\ h]{22\ ^\circ C,\ dark} \underset{92\%}{2(CF_3SO_2)_2NBr} + Hg(SO_3F)_2$$

A slight excess of $Hg[N(SO_2CF_3)_2]_2$ over $BrOSO_2F$ is preferable so that no $BrOSO_2F$ is left unreacted; the latter cannot be readily separated from $(CF_3SO_2)_2NBr$.

To check the generality of the reaction as a new method for the preparation of electropositive *N*-bromo compounds, the previously unknown $Hg[N(SO_2F)_2]_2$ was prepared and found to be equally effective in forming the new compound $(FSO_2)_2NBr$.

$$Hg[N(SO_2F)_2]_2 + 2BrOSO_2F \xrightarrow[10\ h]{22\ ^\circ C,\ dark} \underset{92\%}{2(FSO_2)_2NBr} + Hg(SO_3F)_2$$

These new *N*-bromo sulfonimides are pale yellow liquids at 22 °C, thermally stable in the dark. On exposure to room light at 22 °C in a Pyrex container, the liquids became orange, indicating the formation of bromine. Photolysis under these conditions is slow, resulting in only an ~5% loss of the samples after 3 days.

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The chemical reactivity of the compounds is much greater than the corresponding chlorine analogues. Both *N*-bromo derivatives react with AgCl, forming the respective silver salts and BrCl, and with chloroform, liberating BrCl. As expected, their reactivity does not approach that of $BrOSO_2F$ with covalent chlorides: $BrOSO_2F$ reacts rapidly with $CFCl_3$ at 22 °C, whereas solutions of the new *N*-bromo compounds appear to be stable at 22 °C.

Characterization of the new compounds is given in the experimental section, with the IR, NMR, Raman, and mass spectra being similar to those of the respective analogues $(CF_3SO_2)_2NCl$[11,12] and $(FSO_2)_2NCl$.[13,17,18] Assignment of frequencies to ν_{N-X} in this series is not obvious.

In conclusion, a new method has been found for the preparation of electropositive *N*-bromo derivatives of sulfonimides by reaction of the Hg(II) derivatives with bromine(I) fluorosulfate. The new compounds $(CF_3SO_2)_2NBr$ and $(FSO_2)_2NBr$ should be useful reagents for bromination reactions and for the introduction of the fluoronated sulfonimides into a variety of substrates.

Experimental Section

General Procedures. Reactions and characterizations of compounds were carried out as previously described.[11,19] $BrOSO_2F$,[5] $HN(SO_2F)_2$,[20] and $(CF_3SO_2)_2NH$[11,12] were prepared by literature methods. $Hg[N(SO_2CF_3)_2]$[12] was prepared in an identical manner with that given below for $Hg[N(SO_2F)_2]$, with $(CF_3SO_2)_2NH$ used in place of $HN(SO_2F)_2$.

Preparation of *N*-Bromo Sulfonimides. In a typical preparation, 4.0 g (5.26 mmol) of $Hg[N(SO_2CF_3)_2]_2$ was loaded in a drybox into a 100-mL Pyrex reactor fitted with a glass–Teflon valve. The reactor was then evacuated for 2 h to remove any traces of moisture. The reactor was then cooled to −196 °C, and 1.63 g (9.1 mmol) of $BrOSO_2F$ was added by vacuum transfer. The reactor was allowed to warm to 22 °C and kept at room temperature for 12 h in the dark. The contents of the reactor were agitated by shaking twice during the reaction period. The volatiles were then pumped through a series of cold traps. The −25 °C trap held the desired product $(CF_3SO_2)_2NBr$ (3.02 g, 8.38 mmol) in 92% yield based upon the starting amount of $BrOSO_2F$. A very small amount of Br_2 and a trace of CF_3Br were also recovered.

The preparation of $(FSO_2)_2NBr$ was carried out similarly by using a slight excess of $Hg[N(SO_2F)_2]_2$ over $BrOSO_2F$. Two successive preparations on different scales gave $(FSO_2)_2NBr$ in 91–92% yield.

$(CF_3SO_2)_2NBr$: mp −25 to −24 °C; IR (vapor in equilibrium with liquid, 25 °C) 1459 (s), 1332 (vw), 1242 (vs), 1135 (s), 844 (s), 768 (vw), 640 (w), 599 (ms), 502 (m) cm^{-1}; Raman (solid, −196 °C) 1452 (w), 1248 (vs), 1123 (m), 866 (w), 774 (vs), 643 (m), 574 (vw), 531 (vw), 399 (m), 336 (s), 296 (s), 259 (vs), 171 (ms) cm^{-1}; NMR ($CDCl_3$/$CFCl_3$) −71.9 ppm (s, CF_3); MS, *m/e* (CI/CH_4) 362/360 (MH^+) 100%.

$(FSO_2)_2NBr$: mp −19 to −18 °C; IR (vapor in equilibrium with liquid, 25 °C) 1494 (s), 1236 (s), 897 (s), 830 (s), 646 (m), 561 (s) cm^{-1}; Raman (solid, −196 °C) 1472 (vw), 1445 (vw), 1223 (vs), 926 (w), 835 (m), 650 (ms), 521 (m), 495 (m), 422 (w), 329 (m), 312 (vs), 276 (s), 183 (ms), 173 (m) cm^{-1}; NMR ($CDCl_3$/$CFCl_3$) 53.4 ppm (s, S–F); MS, *m/e* (CI/CH_4) 182 [$(FSO_2)_2NH_2^+$] with Br_2^+ and Br_3^+ as major ions.

Preparation of $Hg[N(SO_2F)_2]_2$. A slight excess of $(SO_2F)_2NH$ (2.40 g, 13.26 mmol) in 10 mL of CF_3CO_2H was added to $Hg(CF_3CO_2)_2$ (2.61 g, 6.12 mmol). The immediate precipitation of $Hg[N(SO_2F)_2]_2$ took place. The reaction mixture was stirred for 20 min at room temperature, and excess CF_3CO_2H was removed under vacuum. The compound was then dried by heating at ~80 °C under vacuum to a constant weight, yielding $Hg[N(SO_2F)_2]_2$ (3.42 g, 6.10 mmol). It is a white hygroscopic solid soluble in CH_3CN and in acetone with reaction to give a brown solution.

$Hg[N(SO_2F)_2]_2$: mp 272 °C dec; IR (solid) 1457 (vs), 1445 (s, sh), 1223 (s), 1196 (s), 1010 (s), 904 (s), 826 (s), 658 (ms), 566 (s), 480 (m) cm^{-1}; NMR (CD_3CN/$CFCl_3$) 52.5 ppm (s, S–F).

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Registry No. $(CF_3SO_2)_2NBr$, 104715-39-1; $(FSO_2)_2NBr$, 104715-40-4; $Hg[N(SO_2CF_3)_2]_2$, 104715-41-5; $Hg[N(SO_2F)_2]_2$, 104693-53-0; $BrOSO_2F$, 13997-93-8; $(SO_2F)NH$, 14984-73-7; $Hg(CF_3CO_2)_2$, 13257-51-7.

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Contribution from the Departments of Chemistry,
University of Tennessee, Knoxville, Tennessee 37996-1600,
and North Carolina State University,
Raleigh, North Carolina 27695-8204

Synthesis, Characterization, and Reactivity of Phosphine- and Arsine-Bridged Dirhodium Complexes Containing Bridging Pyrazolate and Triazolate Ligands

Christopher J. Janke,[†] Louis J. Tortorelli,[†] James L. E. Burn,[†] Craig A. Tucker,[‡] and Clifton Woods*[†]

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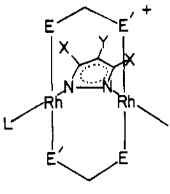
In recent years there has been considerable interest in the synthesis, characterization, and reactivities of dinuclear complexes containing bidentate bridging ligands with group 15[1] donor atoms.[2] Much of this interest is focused on the class of dinuclear species known as A-frame complexes because of the potential of many of these A-frame complexes to act as homogeneous catalysts and add small molecules in the vacant site opposite the bridgehead group.[3] We have been interested in several aspects of new dirhodium A-frame complexes that contain two bridging bis(diphenylphosphino)methane (dppm), bis(diphenylarsino)methane (dam), or (diphenylarsino)(diphenylphosphino)methane (dapm) ligands.

Dinuclear rhodium complexes that contain bridging pyrazolate ligands have been previously reported,[4] but none of these were of the A-frame type that contained two bridging dppm, dam, or dapm ligands and a pyrazolate derivative at the bridgehead until recently when some $(dpm)_2$-bridged dirhodium complexes of this type were reported.[5] This report appeared in the midst of our investigation of this class of compounds, and due to some overlap of these two investigations, we extended our studies to include several additional complexes. We report herein the results of our investigations involving the synthesis and characterization of some additional dppm, dam, and dapm dirhodium A-frame complexes that contain the triazolate (trz), the pyrazolate (pz), the 4-methylpyrazolate (4mpz), and the 3,5-dimethylpyrazolate (35mpz) anions at the bridgehead position. These complexes have the basic structures I–IV and are listed in Table I.



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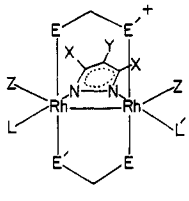
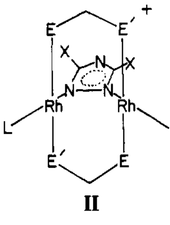


III



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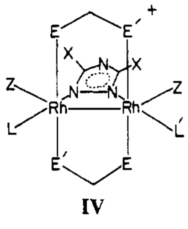

IV

Experimental Section

Materials. Pyrazole (Hpz), triazole (Htrz), 4-methylpyrazole (H4mpz), 3,5-dimethylpyrazole (H35mpz), *n*-BuLi, and *tert*-butyl isocyanide (*t*-BuNC) were obtained from Aldrich Chemicals. $RhCl_3$ was obtained from Johnson Matthey, Inc., and dppm and dam were purchased from Strem Chemicals. Dapm[6] and $[Rh_2(\mu\text{-dppm})_2(CO)_2(\mu\text{-Cl})]PF_6$[7] were prepared according to literature procedures. Tetrahydrofuran (THF) was freshly distilled from sodium and benzophenone.

[†] University of Tennessee.
[‡] North Carolina State University.