The data on methyl radicals[20,23] seem to indicate that this radical reacts with toluenes isoentropically, and a review of the data suggests that all atom transfer processes are approximately isoentropic.[28] If this is true, then the ρ value for any given radical reaction always has the same sign but decreases in absolute value as the temperature is raised.[29] Thus, the positive ρ reported here has significance.

[28] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 100.

[29] Zavitsas in Figure 1, p 7393, ref 18, uses ρ's at different temperatures; clearly this is unwise.[8]

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A Stable Chromium(IV) Alkoxide of a Secondary Alcohol

Sir:

Extensive evidence of the high oxidative power of chromium(IV) toward organic compounds has been obtained in recent years.[1] In the light of these findings it is not surprising that only a few types of reasonably stable organic chromium(IV) compounds are known: tetraalkoxides,[2] tetrakis(dialkylamides),[3] and tetraalkyls.[4,5]

Until now only tetraalkoxides of tertiary alcohols have been known. Attempts to prepare primary and secondary alkoxides by alcoholysis of tetra-*tert*-butyoxychromium(IV)[2] or tetrakis(dialkylamido)chromium(IV) compounds[3] have been unsuccessful, leading instead to clean oxidation of the alcohol to the corresponding aldehyde or ketone. The mechanism of these oxidations presumably consists of a slow exchange reaction yielding primary or secondary chromium(IV) alkoxides as unstable reaction intermediates which then decompose to chromium(III) species and organic oxidation products.

We now wish to report the preparation of the first stable secondary alkoxychromium(IV) compound, tetrakis(3,3-dimethyl-2-butoxy)chromium(IV). In a typical experiment, 0.5 g of tetra-*tert*-butoxychromium(IV)[6] was added to 6 ml of freshly distilled and degassed pinacolyl alcohol, sealed in an ampoule, and heated in a constant temperature bath at 70° for 36 hr.[7] The contents of the ampoule were transferred to a vacuum line where the alcohols were removed leaving a blue solid; mp 63–64°. *Anal.* Calcd for $C_{24}H_{52}O_4Cr$: Cr, 11.4. Found: Cr, 11.3.

A sample was decomposed with methanol, acidified, and analyzed by nmr; pinacolyl alcohol was the only organic compound (besides methanol) which could be detected. The visible spectrum closely resembles that of the tertiary chromium(IV) alkoxides, with a maximum at 608 nm (ϵ 530) and a shoulder at 730 nm (ϵ 350). The magnetic moment is 3.1 BM.

While tetrakis(3,3-dimethyl-2-butoxy)chromium(IV) is very sensitive to both oxygen and moisture, it is remarkably stable in their absence. A solution of the compound (0.02 *M*) prepared from tetra-*tert*-butoxychromium(IV) and an approximately 150-fold excess of 3,3-dimethyl-2-butanol in dioxane showed less than 1% decomposition over 12 hr at 85°. The pure alkoxide has been stored up to 2 weeks in a sealed flask exposed to normal room light without any apparent decomposition. However, the compound is more sensitive to oxygen and moisture than the *tert*-butoxide. Whereas the latter can be dissolved in methanol giving a blue solution which gradually decays with a measurable rate, the secondary alkoxide reacts almost instantaneously, giving the characteristic reduction product, a gray-green insoluble precipitate which is probably chromium(III) trimethoxide.[8]

The difference in stability of *tert*-butyl methyl carbinolate of chromium(IV) and alkoxides of simple primary and secondary alcohols results from the introduction of bulky *tert*-butyl groups. These groups obviously prevent the molecule from achieving the conformation required for hydrogen transfer in the oxidation step.

Acknowledgment. We are grateful for support of this work by the National Science Foundation.

[1] (a) K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, **93**, 2543 (1971); (b) K. B. Wiberg and H. Schäfer, *ibid.*, **91**, 933 (1969); (c) P. M. Nave and W. S. Trahanovsky, *ibid.*, **92**, 1120 (1970); (d) J. Roček and A. E. Radkowsky, *ibid.*, **90**, 2986 (1968); (e) M. Rahman and J. Roček, *ibid.*, **93**, 5455, 5462 (1971).

[2] E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *J. Chem. Soc. A*, 772 (1971).

[3] J. S. Basi, D. C. Bradley, and M. H. Chisholm, *ibid.*, 1433 (1971).

[4] W. Mowat and G. Wilkinson, *J. Organometal. Chem.*, **38**, C35 (1972).

[5] W. Kruse, *ibid.*, **42**, C39 (1972).

[6] H. L. Krauss and G. Münster, *Z. Anorg. Allg. Chem.*, **352**, 24 (1967).

[7] All transfer operations were performed in an inert atmosphere in an efficient glove box.

[8] D. A. Brown, D. Cunningham, and W. K. Glass, *J. Chem. Soc. A*, 1563 (1968).

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Site Selection of Metal Complexation in the Semibullvalene Skeleton. The Exigencies of Palladation

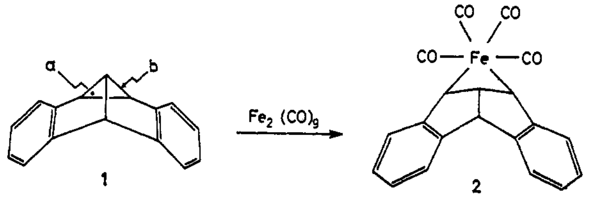
Sir:

It has been recently discovered that the semibullvalene skeleton possesses a remarkable capacity to react with transition metal complexes.[1] Tungsten hexacarbonyl and silver nitrate form weak complexes which merely perturb the fluxional system, leaving the basic skeleton unchanged.[2] Diiron nonacarbonyl is more drastic in its action and prefers to insert iron into carbon–carbon σ-bonds, the favored site apparently being the weakest

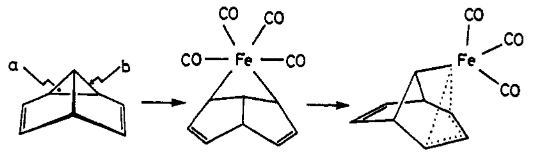
[1] For recent work on complex formation with molecules containing the vinylcyclopropane grouping see: A. D. Ketley and J. A. Braatz, *J. Organometal. Chem.*, **9**, 5 (1967); T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, **33**, 876 (1968); A. Eisenstadt, *Tetrahedron Lett.*, 2005 (1972); R. Aumann, *Angew. Chem.*, **83**, 175, 176, 177 (1971); R. M. Moriarty, C.-L. Yeh, and R. Srinivasan, *Tetrahedron Lett.*, 5325 (1972).

[2] R. M. Moriarty, C.-L. Yeh, E.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **94**, 9229 (1972).

bond of the cyclopropane ring (a).[3] Dibenzosemibullvalene (**1**) gives the simple insertion product ferretane (**2**),[4] whereas the more accommodating parent compound **3** presumably reacts to give the analogous intermediate **4** which subsequently undergoes bond reorganization to give the σ–π-allylic complex **5**.[5] However, two questions arise. The first is how does the rearrangement of **4** proceed, if at all, since the same result could be more economically achieved by direct insertion of iron into the b-bond of the cyclopropane ring.[6] The second question relates to the skeletal change, *i.e.*, why does the bicyclo[3.2.1]octadiene structure result. It appears that the number of sites involved in complexation may play a role. In order to explore this possibility we submitted semibullvalene **3** and its benzo derivative **6** to palladation.



1 2



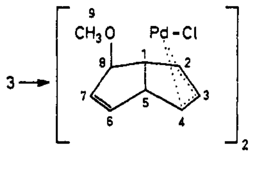
3 4 5

The action of potassium tetrachloropalladate in methanol on **3** and **6** gave in both cases single products, the π-allylic complexes **7** and **8**.[7] The net result is that the a-bond has been oxidatively cleaved to create the bicyclo[3.3.0]octadiene skeleton. The structure proof of **7** and **8** rests on the ^1H and ^{13}C nmr evidence. The values found for **7** are typical of both compounds (Table I). Features which confirm the bicyclo[3.3.0]-octadiene skeleton are the characteristic vicinal coupling constants found for the pairs of protons on C-1 and C-5 and those on C-6 and C-7.[8] The small values found for the vicinal coupling constants exhibited by the C-8 proton provide a strong indication of the exo configuration for the C-8 methoxy group.[8] The complexed trio of carbon atoms (C-2, C-3, and C-4) (and their attached hydrogens) display shifts characteristically shielded ($\Delta\delta\,^{13}C$ = 36–44; $\Delta\delta\,^1H$ = 0.08–0.57 ppm) with respect to those of normal vinyl carbons, *e.g.*, C-6 and C-7.[9]

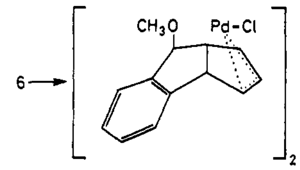
Table I. Nmr Parameters for $(ClPdC_9H_{11}O)_2$ Structure **7**

^{13}C			^1H		
Position	Chemical shifts,[a] ppm	^{13}C–H coupling constants, Hz	Position	Chemical shifts,[a] ppm	H–H coupling constants, Hz
1	55.7	143	1	2.64	J_{15} = 5.0
2	84.2	168	2	5.33	J_{18} = 2.0
3	100.7	183	3	5.75	J_{12} = J_{45} = 1.0
4	84.2	168	4	5.33	J_{23} = J_{34} = 3.0
5	52.6	143	5	3.34	J_{56} = 2.0
6	128.7	168	6	5.90	J_{57} = 2.1
7	136.6	168	7	5.83	J_{67} = 5.8
8	87.9	143	8	4.00	J_{68} = 1.9
9	56.0	147	9	3.30	J_{78} = 2.0

[a] The ^{13}C and ^1H shifts are quoted with respect to $(CH_3)_4Si$ and increasing frequency is taken as positive.



7



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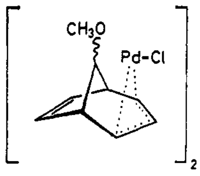

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These findings cast a revealing light on the molecular geometry required for complexation which clearly depends on the nature and number of point attachments needed by the complexed metal atoms. Diiron nonacarbonyl favors the bicyclo[3.2.1]octadiene structure as in this way both the carbon–iron σ-bond and the π-allylic iron bonding are sterically accommodated. On the other hand, palladium(II), which just makes use of a two-point attachment to the π-allylic moiety, selects the sterically less encumbered bicyclo[3.3.0] structure. Attempts to make palladium π-allylic complexes from bicyclo[3.2.1]octene derivatives have failed so far, presumably on account of excessive encumbrance on both faces of the molecule. Accordingly such complexes, *e.g.*, **9**, do not form.[10]

Thus it may be predicted that semibullvalene on complexation with transition metals will collapse to that particular member of the C_8H_8 family which fits the steric and electronic exigencies for satisfactory bonding. A knowledge of the stepwise process by which the final structure is attained is not presently

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(3) R. Hoffmann, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., 1971, Special Lectures, Vol. 2, Butterworths, London, p 233; R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971).

(4) R. M. Moriarty, K.-N. Chen, C.-L. Yeh, J. Flippen, and J. Karle, *J. Amer. Chem. Soc.*, **94**, 8944 (1972).

(5) R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971); R. Aumann, *Angew. Chem.*, **84**, 583 (1972).

(6) (a) A similar intermediate has been postulated for the reaction of cyclopropylstyrenes with iron pentacarbonyl: S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Amer. Chem. Soc.*, **87**, 2517 (1965). (b) The hypothetical intermediate **4** could undergo a [1,3] sigmatropic shift to give **5**; however, such a rearrangement cannot operate for the analogous complex derived from **6**.

(7) (a) Complex **7** obtained in 75% yield had mp 78° dec. *Anal.* Calcd for $C_9H_{11}OPdCl$: C, 38.61; H, 3.92; Cl, 12.77. Found: C, 38.41, H, 3.89, Cl, 12.98. Complex **8** obtained in 80% yield had mp 162° dec. *Anal.* Calcd for $C_{13}H_{13}OPdCl$: C, 47.72; H, 3.98; Cl, 10.86. Found: C, 47.60, H, 4.04; Cl, 10.84. (b) When the vinyl moiety is entirely absent, as in **1**, no reaction occurs.

(8) R. M. Moriarty and C.-L. Yeh, *Tetrahedron Lett.*, 383 (1972).

(9) B. E. Mann, R. Pietropaolo, and B. L. Shaw, *Chem. Commun.*, 791 (1971); L. F. Farnell, E. W. Randall, and E. Rosenberg, *ibid.*, 1078 (1971).

(10) Attempts to make the π-allylic complexes of *exo*-3,4-dibromobicyclo[3.2.1]oct-2-ene and its 1-methyl derivative failed.

known, but it is seen that the number of attachments, bipodal, tripodal, etc., largely determines the ring type within the limits imposed by the molecular formula.

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(11) Invited Professor at the University of Geneva.

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Disulfur Binuclear Ruthenium Ammines

Sir:

In the course of earlier work[1] with sulfur-containing ligands (*e.g.*, thiophene, thiosulfate) reacting with ruthenium ammines, a green color was frequently observed, but the species responsible for the color was not identified. We have now established the stoichiometry and some features of the structure of a green cation containing ruthenium, sulfur, and ammonia. The species we have characterized is remarkably stable and can be produced in a variety of ways. The ion, which we take to be $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ (I) represents a novel bonding mode for sulfur to metal ions,[2] and because of the simplicity of its composition and presumably of its structure, the chemistry of I and of related species offers an opportunity for improving the basic understanding of sulfur as a ligand.

The green ion has been produced in three different ways: (1) by the action of the sulfurizing agents C_2H_4S and COS on $(NH_3)_5RuH_2O^{2+}$, (2) by reducing $(NH_3)_5RuSO_2{}^{2+}$ with amalgamated zinc, (3) by oxidizing a mixture of $(NH_3)_5RuH_2O^{2+}$ and H_2S. It is of interest to note that oxidation of $(NH_3)_5RuSR_2{}^{2+}$ or $(NH_3)_5RuSHR^{2+}$ does not produce the green ion, except for trace amounts in the second case.

Typical preparative procedures following methods 1 and 2 are herewith described.

In method 1, the preparation of $[(NH_3)_5RuS]_2Br_4$ (II), a slurry of 0.3 g of $[(NH_3)_5RuCl]Cl_2$ in 18 ml of H_2O was reduced with amalgamated zinc under argon for about 45 min. The solution containing $[(NH_3)_5RuOH_2]^{2+}$ was then transferred under Ar into a vessel with 25 ml of methanol and 2 ml of ethylene sulfide. The reaction mixture was kept under argon for about 30 min. Methanol and excess of episulfide were removed by vacuum distillation. The solution was filtered from polymerization products of episulfide and 3 ml of saturated NH_4Br solution was added. After the solution was cooled, a precipitate of dark fine needles was collected. This product usually was contaminated by organic impurities and was recrystallized three times. *Anal.* Calcd for $[(NH_3)_5RuS]_2Br_4 \cdot 2H_2O$: Ru, 25.5; N, 17.7; H, 4.3; S, 8.1; Br, 40.3. Found: Ru, 24.9; N, 17.8; H, 4.1; S, 8.4; Br, 39.6 (analysis for Ru by residue; values obtained in this way are somewhat inaccurate). The chloride salt can be prepared by a similar method.

In method 2, the preparation of *trans*-$[Cl(NH_3)_4RuS]_2Cl_2$ (III), an amount (150 mg) of *trans*-$[(NH_3)_4RuSO_2Cl]Cl$ was dissolved in 10 ml of 0.05 *M* HCl. The solution was cooled in ice, and several pieces of amalgamated zinc were added to it. As the solution was stirred in air, it gradually turned green and after 15–20 min it was filtered and charged onto a cation exchange column (Bio-Rad AG 50W-X2 200–400 mesh, hydrogen ion form). The resin was eluted first with 0.25 *M* NaCl which carried along a species resembling the starting material. After this stage, the column was washed with 0.05 *M* HCl. These treatments left a dark green band at the top of the column which moved slowly with 0.9 *M* HCl and more rapidly with 1.6 *M* HCl. The green solution was collected and concentrated by rotary evaporation. After cooling overnight at −5°, a black-green solid formed. This was collected, washed with ethanol and diethyl ether, then dried in a vacuum desiccator. More of the product was obtained by treating the first eluent as has been described, total yield 60 mg. *Anal.* Calcd for $[Cl(NH_3)_4RuS]_2Cl_2 \cdot 1.5H_2O$: S, 11.21; H, 4.72; N, 19.61; Cl, 24.87; Ru, 35.4. Found: S, 11.18; H, 4.25; N, 19.69; Cl, 25.05; Ru, 35.3 by atomic absorption, 33.35 by residue (the compound is hydroscopic). The positions trans to the disulfur group appear to be fairly labile; taking advantage of this fact, the compound [isonicotinamide-$(NH_3)_4RuS]_2Br_4$ (IV) was prepared. *Anal.* Calcd for the dihydrate: Ru, 20.2; C, 14.4; N, 16.8; H, 4.0. Found: Ru, 20.0; C, 13.82; N, 16.4; H, 3.58.

The ion exchange behavior of a solution of II, comparing the elutability with ions of known 4+ charge, indicates that the cation contained in II also carries a 4+ charge. Measurements of the magnetic susceptibility of II show it to have a small positive value, corresponding to 0.45 BM per dimer at 25°, but independent of temperature over the range 25 to −100°. For III, the magnetic susceptibility at room temperature (22–24°) corresponds to 1.1 BM per dimer. A solution of III in D_2O (0.1 *M* DCl) shows a single proton nmr signal, at 3.10 ppm referred to trimethylsilyl propionate, having within 10% the intensity expected for the octaammine formulation. No esr signal was observed for III dissolved (0.01 *M*) in water even on cooling to liquid nitrogen temperatures. The Raman spectrum of II dissolved in H_2O, taken with a Spex 1401 spectrometer using 488 nm as the exciting line, shows a band at 519 ± 2 cm^{-1}. This can be compared to the S–S stretching frequency in H_2S_2, dialkyl disulfides, and disulfur halides at 509, 495–520, and 510–540 cm^{-1}, respectively. The band at 519 cm^{-1} is absent from the ir spectrum and is unshifted on deuteration of the complex. The diaquooctaammine, dichlorooctaammine, and the diisonicotinamideoctaammine ions show Raman bands at 515 ± 3, 520 ± 3, and 526 ± 3 cm^{-1}.

The results quoted support structure I for the green ion present in II. The cations present in III and IV are taken to have molecules of Cl^- or isonicotinamide occupying coordination positions on Ru, trans to sulfur.

The spectrum of a solution of II is shown in Figure 1.

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[1] J. N. Armor and H. Taube, unpublished observations.

[2] Other examples of the disulfur group bridging metal atoms have been reported: *cf.* C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965); D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 3727 (1967); G. T. Kubas, T. G. Spiro, and A. Tirzes, *ibid.*, **95**, 273 (1973). In all of these cases, the metal centers are connected by other bonds as well.