or Me resonances. (2) Irradiation of H_B results in large enhancement of the H_A resonance and lesser enhancement of the Cp and phenyl resonances. (3) Irradiation of the Me resonance resulted in enhancement of the H_A, Cp, and part of the phenyl multiplet. (4) Irradiation of the Cp resonance resulted in enhancements of the H_B, Me, and *o*-phenyl resonances but in a *negative* NOE for the H_A resonance. (5) Irradiation of the *o*-phenyl multiplet resulted in enhancements of the H_A, H_B, and Cp resonances, but not in the Me resonance.

In a spin system such as that under consideration here, all nuclei can in principle experience dipolar relaxation by (and hence gain NOE from irradiation of) all other nuclei, the relative effects being inversely proportional to the sixth power of the distance between pairs of nuclei.[10–13] The fact that the two α-hydrogen atoms gain almost as much total enhancement from irradiation of the Cp, Me, and phenyl resonances as they do from irradiation of their geminal partner demonstrates this fact. It is also to be expected that the Cp and PPh_3 ligands may well be undergoing rotational motions which are rapid relative to the various dipolar relaxation rates, and it becomes clear that a comprehensive description of the NOED experiments in terms of molecular geometry is a far from trivial task.

However, if one assumes that the rapidly rotating Cp group can be treated as a net dipole acting from the mean of all possible orientations (see ref 13 for similar treatment of rapidly rotating methyl groups), then the question of orientation of the alkyl ligand becomes answerable. The key lies in the experiment (Figure 1e) which involves irradiation of the Cp resonance, where a large, positive enhancement was observed for the H_B resonance, but a small, negative NOE was observed for the H_A resonance. This type of behavior is uniquely characteristic of three-spin systems in which the three nuclei in question are aligned in a more or less linear fashion and provides direct evidence that the Cp–H_B–H_A assemblage defines an obtuse angle.[11–13] This conclusion is reinforced by the observation of a positive NOE for the Cp resonance on irradiation of H_B (Figure 1c) but not on irradiation of H_A (Figure 1b), suggesting that the former is indeed closer to the Cp group. These results are clearly incompatible[15] with a conformation such as **3** and appear to be most consistent with conformations such as **1** ($\simeq$**4**) or **2** (which can probably be ruled out because of the close proximity of the bulky groups L, R, and Cp.

As discussed above, however, our earlier variable-temperature NMR data for compounds of the type I are generally best interpreted in terms of a most stable rotamer having one large and one small ^3J(P–H), a conclusion inconsistent with both **1**, which should exhibit two small (gauche) coupling constants, and **4**, which should exhibit one small (gauche) and one almost zero (90°) coupling constant. While we had originally assumed staggered energy minima such that the large and small vicinal coupling constants are to be related to antiperiplanar and gauche couplings,[6] respectively, it now seems that the assumption of a maximum degree of staggering was not warranted. The conformation most consistent with the NOED and variable-temperature coupling constant data *and* the EH calculations is **5**, with the large vicinal coupling constant to be attributed to an α-hydrogen atom which is eclipsed or nearly eclipsed with the phosphorus atom and the small coupling constant to a hydrogen atom which is gauche to or possibly at approximately a 90° angle with the phosphorus. Thus R preferentially occupies a position which places it as far as possible from both the Cp and the L groups, a conclusion which is supported by molecular models.[16]

The relative chemical shifts of H_A and H_B are also consistent with **5** being a good approximation to the low-energy conformation. The difference between the two, 1.01 ppm, with the higher field resonance being assigned to the α-hydrogen atom eclipsing the PPh_3, is most consistent with the latter (H_A) being strongly affected by the ring current[17] of the aryl rings. This conclusion is quite consistent with the conformation illustrated as **5**, as H_A would spend on average considerable time close to a face of a phenyl ring.[18]

The remaining NOE data cannot unfortunately be interpreted in terms of relative internuclear distances, in part because the total NOE's have not been fully developed, in part because of the averaging effects related to rotation about the Cp–Fe, the P–aryl, and the Fe–P bonds. Various other "three-spin" sets of mutually relaxing nuclei must also be present, leading to alterations in enhancements. However, it seems clear that most of the pairs of the ligand hydrogen atoms effect mutual dipolar relaxation, consistent with their being resonably contiguous in space, i.e., with the above-mentioned rotations and the probable degree of steric congestion.

The approach to conformational analysis of flexible organometallic compounds described here would appear to have wide utility. Experiments to determine the NOE growth rates are expected to provide information on internuclear distances[11] and are in progress.

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Registry No. I (R = $SiMe_3$), 32761-84-5.

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[15] Reference 12, p 77.

[16] The alternate "eclipsed" structure, involving eclipsing of the other methylene hydrogen atom with L, can be ruled out on the basis of both anticipated steric effects and the NOED data.

[17] Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969, p 64.

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Binuclear Carbonylates $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$: Syntheses and Crystal Structures

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Summary: The new dianion $[Ru_2(CO)_8]^{2-}$ has been prepared from the reaction of CO_2 with $[Ru(CO)_4]^{2-}$ in a 1:1 molar ratio. In a similar manner $[Os_2(CO)_8]^{2-}$ has been prepared. X-ray crystal structures of tetraphenylphosphonium salts of these ions have been determined. The structure of $[Ru_2(CO)_8]^{2-}$ represents a previously unobserved and apparently unanticipated configuration for homodinuclear carbonylates and carbonyls. It consists of a trigonal-bipyramidal fragment ($Ru(CO)_4$) joined to a four-sided pyramidal fragment ($Ru(CO)_4$). The structure of $[Os_2(CO)_8]^{2-}$ is like that of $[Fe_2(CO)_8]^{2-}$.

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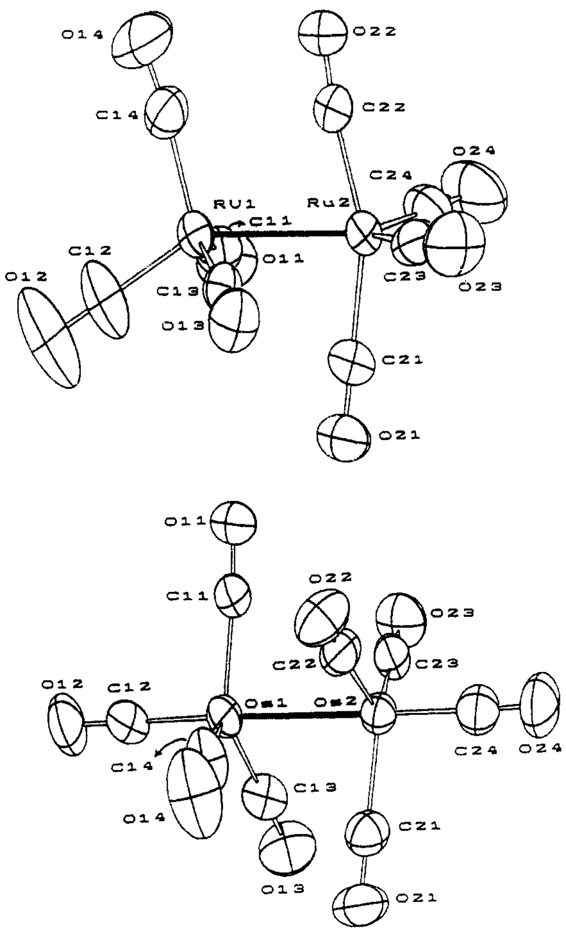

Figure 1. Structures of $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$.

The binuclear carbonylate $[Fe_2(CO)_8]^{2-}$ has been well characterized chemically[1-3] and structurally.[4] Of the related dianions however, $[Ru_2(CO)_8]^{2-}$ has not been reported previously while the preparation of $[Os_2(CO)_8]^{2-}$ has been inferred from the preparation of diosmacycloalkane derivatives.[5] It is of interest to provide a practical route to these anions in view of the rich derivative chemistry of the $[Fe_2(CO)_8]^{2-}$ analogue. Furthermore, the structures of these anions are of considerable interest in view of variations observed[4] in molecular geometry among the isoelectronic species $[Fe_2(CO)_8]^{2-}$, $[FeCo(CO)_8]^{1-}$, and $Co_2(CO)_8$. Reported here is the preparation, isolation, and crystal structures of $[P(C_6H_5)_4]_2[Ru_2(CO)_8]\cdot CH_3CN$ and $[P(C_6H_5)_4]_2[Os_2(CO)_8]\cdot {}^2/_3CH_3CN$.

Our synthetic procedures are based upon the following sequence of reactions in which half of the available starting material $[M(CO)_4]^{2-}$ is converted to $M(CO)_5$[6] which in turn reacts with the remaining $[M(CO)_4]^{2-}$ to form $[M_2(CO)_8]^{2-}$.

$$2[M(CO)_4]^{2-} + 2CO_2 \rightarrow [M(CO)_4]^{2-} + M(CO)_5 + [CO_3]^{2-}$$

$$[M(CO)_4]^{2-} + M(CO)_5 \rightarrow [M_2(CO)_8]^{2-} + CO$$

$$M = Ru \text{ or } Os$$

Suitable crystals for X-ray analysis were obtained by slow diffusion of $(C_2H_5)_2O$ into CH_3CN solutions of the tetraphenylphosphonium salts of the dianion. The structures of these dianions are shown in Figure 1.[7] The $[Ru_2(CO)_8]^{2-}$ ion is of C_s point symmetry while that of $[Os_2(CO)_8]^{2-}$ is of D_{3d} point symmetry like that[4] of $[Fe_2(CO)_8]^{2-}$.

The structure of $[Ru_2(CO)_8]^{2-}$ represents a previously unobserved and apparently unanticipated configuration for homodinuclear carbonylates and carbonyls. The structure consists of a trigonal-bipyramidal fragment bound to a four-sided pyramidal fragment. The trigonal-bipyramidal fragment contains Ru(2) as the central atom, with the Ru(1) atom bound at an equatorial site. The Ru(2) atom also resides at the basal site of a shallow four-sided pyramid for which Ru(1) is the central atom and C(14)–O(14) is the apical ligand. There are two least-squares planes associated with $[Ru_2(CO)_8]^{2-}$ (Figure 1) which are of interest in that they show the spatial relationship between the two $Ru(CO)_4$ units. The dihedral angle between these planes is 90.3°. The vertical plane is the mirror plane of the molecule. It passes through the axial positions (C(21), C(22)), the central atom Ru(2), and the equatorial position (Ru(1)) of the trigonal-bipyramidal fragment. This plane also passes through the apical position (C(14)), the central atom Ru(1), and the basal positions (C(12), Ru(2)) of the four-sided pyramidal fragment. The largest deviation from this vertical plane is shown by Ru(2), 0.061 Å. The horizontal least-squares plane passes through the equatorial atoms (C(23), C(24), Ru(1)) and the center (Ru(2)) of the trigonal-bipyramidal fragment. The largest deviation from this horizontal plane is shown by Ru(2), 0.062 Å.

Bond angles around the apical carbon (C(14)) of the four-sided pyramidal fragment are C(14)–Ru(1)–C(11) = 109.6 (4)°, C(14)–Ru(1)–C(12) = 105.5 (5)°, C(14)–Ru(1)–C(13) = 107.2 (4)°, and C(14)–Ru(1)–Ru(2) = 105.1 (3)°. On the trigonal-bipyramidal fragment, the angle between the equatorial sites on Ru(2) is C(23)–Ru(2)–C(24) = 112.7 (5)°. Axial carbonyls on Ru(2) are tipped over the Ru(1)–Ru(2) bond[8] with acute angles of Ru(1)–Ru(2)–C(21) = 82.6 (3)° and Ru(1)–Ru(2)–C(22) = 74.5 (3)°. Respective Ru(2)–C–O angles involving these carbonyls indicate essentially linear arrangements: 179.4 (8)° and 173.2 (8)°. Two of the carbonyls on Ru(1) are also tipped over the Ru(1)–Ru(2) bond with angles of Ru(2)–Ru(1)–C(11) = 78.0 (3)° and Ru(2)–Ru(1)–C(13) = 76.3 (2)°. The Ru(1)–C–O angles for these respective bonds are 174.7 (9)° and 175.9 (7)°. Similar tipping of terminal carbonyls without significant decrease of the metal–C–O angle has

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Crystal data for $[P(C_6H_5)_4]_2[Ru_2(CO)_8]\cdot CH_3CN$: space group Cc, a = 19.454 (2) Å, b = 16.672 (1) Å, c = 16.349 (4) Å, β = 98.74 (2)°, V = 5240.8 Å^3, ρ(calcd) = 1.452 g cm^{-3} for M_r = 1146.08 and Z = 4, μ(Mo Kα) = 6.78 cm^{-1}. R_F = 0.030 and R_{wF} = 0.039 for 3271 reflections [$I > 3.0\sigma(I)$] of 5005 reflections collected in the range of $4° < 2\theta < 50°$.

Crystal data for $[P(C_6H_5)_4]_2[Os_2(CO)_8]\cdot {}^2/_3CH_3CN$: space group $P\bar{1}$, a = 16.677 (2) Å, b = 22.127 (2) Å, c = 11.154 (1) Å, α = 90.885 (9)°, β = 105.02 (1)°, γ = 77.79 (1)°, V = 3880.9 Å^3, ρ(calcd) = 1.682 g cm^{-3} for M_r = 1324.34 and Z = 3, μ(Mo Kα) = 50.22 cm^{-1}. R_F = 0.027 and R_{wF} = 0.035 for 8671 reflections [$I > 3.0\sigma(I)$] of 14 398 reflections collected in the range of $4° < 2\theta < 50°$.

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been observed in saturated[4] and unsaturated dinuclear carbonyls.[8,9] The bond distance Ru(1)–Ru(2) = 2.936 (1) Å. Ru–C distances are 1.938 (9)–1.836 (10) Å, and the Ru–C–O angles are 179.4 (8)–172.7 (1)°. The closest intermolecular distance observed is 3.075 (6) Å, between the methyl carbon of CH_3CN and O(12).

The structure of the $[Os_2(CO)_8]^{2-}$ dianion is like that of $[Fe_2(CO)_8]^{2-}$.[4] It can be viewed as two $Os(CO)_4$ units with CO's at four vertices of a trigonal bipyramid with the fifth vertex being an axial site common to both $Os(CO)_4$ units. The equatorial planes are staggered with respect to each other. As in $[Fe_2(CO)_8]^{2-}$, each equatorial CO is tilted toward the opposite metal.[4] The angle of tilt, M–M–C, is in the range 80.5 (2)–87.0 (2)°. Metal–metal distances for the independent molecules in the unit cell are Os(1)–Os(2) = 2.992 (1) Å and Os(3)–Os(3′) = 2.985 (1) Å. The Os–C distances are 1.917 (6)–1.867 (6) Å, and the Os–C–O angles are 178.8 (6)–174.9 (6)°. The closest intermolecular distance observed is 3.042 (10) Å, between a phenyl carbon of the cation (C(246)) and O(14).

The salt $Na[Ru_2(CO)_8]$ was prepared from the reaction of a 1:1 molar ratio of $Na_2[Ru(CO)_4]$ (264.3 mg) and CO_2 (1.02 mmol) in THF (15 mL), stirred overnight at −78 °C and then for 4–5 h at room temperature. A pale red solution formed, and the theoretical amount of CO was produced. The resultant $Na_2[Ru_2(CO)_8]$ was converted to $[P(C_6H_5)_4]_2[Ru_2(CO)_8]$, a pale yellow solid, in about 90% yield by metathesis of $Na_2[Ru_2(CO)_8]$ with $[P(C_6H_5)_4]Br$ in THF. $[P(C_6H_5)_4]_2[Ru_2(CO)_8]$: IR ($CH_3CN$) ν(CO) 1930, 1865 cm^{-1}; ^{13}C NMR (CH_3CN, +30 to −35 °C) 215.1 ppm.

Reaction of $K_2[Os(CO)_4]$ with CO_2 in a 1:1 molar ratio in THF overnight at −78 °C and then at 60 °C for 48 h produced a solution of $K_2[Os_2(CO)_8]$. The salt $[P(C_6H_5)_4]_2[os_2(CO)_8]$ was obtained as a yellow solid in 55% yield in the same manner as indicated above. $[P(C_6H_5)_4]_2[Os_2(CO)_8]$: IR ($CH_3CN$) ν(CO) 1940, 1865 cm^{-1}; ^{13}C NMR (CH_3CN, 30 to −35 °C) 193.5 ppm.

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Supplementary Material Available: Listing of positional parameters, anisotropic thermal parameters of non-hydrogen atoms, selected bond distances and bond angles, least squares planes and dihedral angles, and structure factor amplitudes (113 pages). Ordering information is given on any masthead page.

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Preparation and Reactivity of Mononuclear (η^5-Cyclopentadienyl)cobalt Carbene Complexes

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Summary: (η^5-C_5H_5)Co(CO)$_2$ reacts with bis(1,3-dimethylimidazolin-2-ylidene) to furnish the first mononuclear cyclopentadienylcobalt carbene complex **1**. Complex **1** reacts with several electrophilic reagents including Ph_2S_2 to produce the structurally characterized paramagnetic cyclopentadienylcobalt carbene complex **4**.

Since the discovery of the first transition-metal carbene complex $(CO)_5W[C(OCH_3)CH_3]$ by Fischer and Maasböl in 1964,[1] there has been an ever increasing interest in the preparation, structure, and reactivity of new transition-metal carbene complexes.[2] Diamagnetic carbene complexes are known for nearly all the transition metals; in contrast, there are relatively few paramagnetic carbene complexes including derivatives of iron,[3] chromium,[4] and ruthenium.[5] This report describes the preparation and reactivity of several mononuclear cyclopentadienylcobalt carbene complexes including the isolation of a paramagnetic cobalt carbene complex (**4**) which has been characterized by single-crystal X-ray diffraction methods.

Several mononuclear cobalt carbene complexes are known,[6] but surprisingly, no carbene complexes derived from (η^5-C_5H_5)Co(CO)$_2$ have been reported, even though this compound has been known for over 30 years.[7] Dinuclear bridging carbene complexes of cobalt have, however, been prepared from the reaction of (η^5-C_5H_5)Co(CO)$_2$ with diazo compounds.[8]

Treatment of (η^5-C_5H_5)Co(CO)$_2$ with bis(1,3-dimethylimidazolindin-2-ylidene) in boiling methylcyclohexane produced **1** as red-brown crystals.[9] Quantities up to 5 g have been prepared in yields ranging from 60 to 75%. In most cases complex **1** crystallizes analytically pure from the reaction mixture. This cobalt carbene is extremely air-sensitive as a solid and in solution but exhibits good thermal stability in a nitrogen atmosphere. No reaction occurred between **1** and Ph_3P in boiling toluene during a 24-h period (>90% recovery of **1**). Complex **1** shows a very low-energy metal carbonyl band in the infrared spectrum at 1915 cm^{-1} (pentane). This value is one of the lowest metal carbonyl bands observed for complexes of the type (η^5-C_5H_5)Co(CO)L. Complexes with similar values include (η^5-C_5H_5)Co(CO)(PMe$_3$) (1923 cm^{-1}, pentane)[10] and (η^5-C_5Me_5)Co(CO)(PMe$_3$) (1915 cm^{-1}, hexane).[11] This sug-

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