sertion" and addition products produced by the reaction of the carbalkoxycarbene with allyl chlorides. The benzophenone-sensitized photodecomposition of dimethyl diazomalonate in allyl chloride resulted in 88% addition and a trace of "insertion" product (see Table II).

Table II. Benzophenone-Sensitized Decomposition of Diazocarbonyl Compounds in Allyl Halides

Diazo compd	Halide	Insertion,[d] %	Addition,[e] %
DM[a]	$CH_2{=}CHCH_2Cl$	5	88
DM	$CH_2{=}C(CH_3)CH_2CH_2Cl$	Trace	86
DM	$CH_3CH{=}CHCH_2Cl$	Trace	49
DM	$CH_2{=}CHCH_2Br$[f]	4	30
DA[b,c]	$CH_2{=}CHCH_2Cl$	7	69
DA	$CH_2{=}C(CH_3)CH_2Cl$	6	85
DA	$CH_3CH{=}CHCH_2Cl$	3[g]	22

[a] Dimethyl diazomalonate. [b] Ethyl diazoacetate. [c] Direct absorption of light by ethyl diazoacetate itself could not be completely neglected. [d] Allyl halide insertion product. [e] Olefin double bond addition. [f] 35% of dimethyl bromomalonate was also obtained. [g] Mixtures of α- and γ-methylallyl chloroethylacetate.

The attractive mechanism (eq 1) for the "insertion" product through the halonium ylide intermediate may be supported by the following evidence. In direct photolysis, the "insertion" reaction with allyl chloride was about 1~2.5 times faster than the addition, whereas with allyl bromide it was about 8 times faster than addition.[11] Since the reactivities of the double bonds toward the attacking carbene species are not considered to be very different in these two allylic substrates, the change in the ratio of "insertion" to addition may be due to the difference in nucleophilicity between a chlorine and a bromine atom. This consideration is supported by the results which were obtained by competitive experiments using pairs of allylic compounds.

Table III compares the relative rates of "insertion" and addition of singlet and triplet bis(carbomethoxy)carbene to the allyl halides and ethyl allyl sulfide. The data indicate that the singlet carbene attacks bromine and sulfur atoms about two times faster than it attacks a chlorine atom in an allylic position, as is expected from the electrophilic nature of the attacking carbene. On the other hand, the singlet carbene, as well as the triplet carbene, adds to the double bond at almost equal rates irrespective of the nature of the allylic substrate.

Table III. Competitive Reactions of Singlet and Triplet Bis(carbomethoxy)carbene to Allyl Compounds

Allyl compd	Singlet I	Triplet I
Allyl chloride	a,[a] 1 (standard)	a, 1 (standard)
	i,[b] 2.3	i, 0.07
Allyl bromide	a, 1.0	a, 1.0
	i, 8.5[c]	i, 0.3
Ethyl allyl sulfide	a, 1.2	a, 1.0
	i, 6.3	i, 0.5

[a] a, addition product. [b] i, "insertion" product. [c] The product was unstable to prolonged irradiation.

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A Rhodium(II)-to-Rhodium(II) Single Bond in Bis(triphenylphosphine)tetrakis(dimethylglyoximato)dirhodium

Sir:

In recent years it has been recognized that metal-to-metal bond formation occurs widely in transition metal compounds, and that the bonds vary considerably in strength.[1-3] Extremely short bonds of high multiplicity[3] are in some ways the easiest to understand, whereas the longer, lower order bonds show considerable variations in length which are not always easy to explain. Just because these longer bonds are weaker, their lengths are very sensitive[3] to factors such as the bulk and electronegativities of ligands, formal the oxidation state of the metal, and the geometric constraints imposed by bridging ligands when these are present.

Rhodium in its lower oxidation states apparently affords a variety of species containing Rh–Rh bonds. Several carbonyls ($Rh_6(CO)_{16}$, Rh–Rh 2.776 Å[4]) and cyclopentadienyl carbonyls ((h^5-$C_5H_5)_2Rh_2(CO)_3$, Rh–Rh = 2.68 Å;[5] (h^5-$C_5H_5)_3Rh_3(CO)_3$, Rh–Rh = 2.62 Å[6]) have been studied structurally as has the Rh(II) compound $Rh_2(O_2CCH_3)_4 \cdot 2H_2O$, for which only a rough structure with Rh–Rh ≈ 2.45 Å is reported.[7] Recently several new dinuclear Rh(II) compounds have been prepared, *e.g.*, $Rh_2(DMG)_4(P(C_6H_5)_3)_2$[8] (DMG = monoanion of dimethylglyoxime) and $Rh_2^{4+}(aq)$.[9] We have succeeded in obtaining a suitable crystalline form of the first of these and have determined its structure by X-ray diffraction in order to see what degree of metal-to-metal bonding might be present.

Crystals, grown from a solution in propanol containing a little H_2O, with the stoichiometry $Rh_2(C_4H_7N_2O_2)_4[P(C_6H_5)_3]_2 \cdot H_2O \cdot C_3H_7OH$, belong to the monoclinic system; space group, $P2_1/c$; a = 18.695 (6), b = 13.417 (5), c = 22.817 (7) Å, β = 98.53°. The above formula represents the asymmetric unit of which there are four per unit cell. The structure was solved by direct methods and refined by full-matrix least squares, with the phenyl groups treated as rigid bodies. Approximately 3300 reflections whose intensities were $\geq 2\sigma$ (the esd based on counting statistics), collected within a sphere with 2θ = 40° (Mo Kα), were employed. The Rh and P atoms were refined anisotropically. The final value

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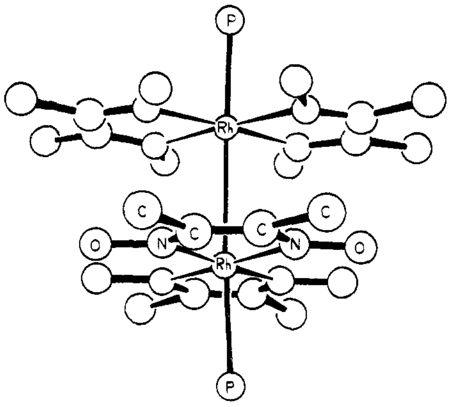

Figure 1. The structure of $Rh_2(DMG)_4(P(C_6H_5)_3)_2$. The phenyl groups are omitted for clarity.

of the usual discrepancy index, $R_1 = \Sigma||F_c| - |F_o||/\Sigma|F_o|$, was 0.085.

The $Rh_2(DMG)_4(P(C_6H_5)_3)_2$ molecule, with the phenyl groups omitted, is depicted in Figure 1. Its most prominent and important structural feature is the Rh–Rh bond, unsupported by bridging groups, with a length of 2.934 (2) Å. The molecule as a whole possesses no rigorous crystallographic symmetry; however, neglecting the phenyl groups, it has very nearly D_{2d} symmetry. The Rh–Rh–P angles are 176.8 (3)°, the two $Rh(DMG)_2$ units are each essentially planar, and the two such planes are virtually parallel to each other and perpendicular to the Rh–Rh axis. One $Rh(DMG)_2$ unit is rotated about the Rh–Rh axis by 92 ± 1° relative to the other. The Rh–N distances range from 1.95 (2) to 2.03 (2) Å with a mean of 1.99 Å, while the Rh–P distances are 2.447 (5) and 2.430 (5) Å.

We believe that this molecule displays an Rh–Rh single bond probably somewhat elongated by repulsive interactions between the parallel pairs of DMG ligands. There are marked similarities to the $Ni(DMG)_2$, $Pd(DMG)_2$, and $Pt(DMG)_2$ structures,[10,11] which consist of parallel infinite chains of planar molecules stacked perpendicular to their planes with each molecule rotated 90° to its chain neighbors. The interplanar spacings in these cases are ~3.24 Å. Even this distance is slightly less than the expected van der Waals contact distance and, together with other evidence, suggests weak M–M attractive forces. The mean interplanar distance of 2.91 Å (essentially equal to the Rh–Rh distance, 2.93 Å) in the dinuclear Rh compound shows that there is a substantial Rh–Rh bond, which would presumably be even shorter were it not opposed by the ligand–ligand repulsions. That the Rh–Rh bond must be essentially a single, two-electron σ bond follows from the fact that for Rh(II) the 7 d electrons in the $Rh(DMG)_2(P(C_6H_5)_3)$ moiety can only reasonably be allocated so as to leave one σ electron in an orbital directed opposite to the Rh–P bond. Overlap of two such orbitals then forms a single, σ Rh–Rh bond, just as a single, σ Rh–Cl bond is formed in $ClRh(DMG)_2P(C_6H_5)_3$.

Even allowing for several tenths of an angstrom lengthening of this Rh–Rh bond by repulsions, it seems clear that the Rh–Rh distance, ~2.45 Å, in $Rh_2(O_2CCH_3)_4(H_2O)_2$ is short enough to imply a multiple interaction as previously proposed by us.[12]

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Preparation and Crystal Structure of a Sterically Unencumbered Tetrahedral Chelate Complex Containing a NiS_4 Core, $[SPMe_2NPMe_2S]_2Ni^{II}$

Sir:

A large body of elegant experimental work has been performed in an effort to ascertain the factors which dictate the stereochemistry of metal(II) chelate complexes. These approaches[1–5] have employed bidentate chelates in which either the donor functions or the degree of crowding can be changed. Monomeric sterically unencumbered[5] chelates of nickel(II) with various permutations of donor sets (NR, S, O) have been found to be planar ($S = 0$), while those which are sterically overcrowded are either fully tetrahedral ($S = 1$) or are involved in a planar $\rightleftharpoons$ tetrahedral equilibrium in solution. Significantly, all known monomeric Ni(II) chelates with four coordinated sulfur atoms are diamagnetic and have been shown to be planar either from crystallographic studies[6] or by inference from magnetic and optical spectral studies.[7]

We now wish to report the preparation and crystallographic characterization of $[SPMe_2NPMe_2S]_2Ni^{II}$, a sterically unencumbered complex in which a Ni(II) ion is coordinated to four sulfur atoms, yet adopts a *tetrahedral* configuration.

The reaction of $Na^+[SPMe_2NPMe_2S^-]$[8,9] with $[Et_4N]_2[NiCl_4]$ in absolute methanol followed by recrystallization from dichloromethane–heptane yields olive

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