pairs. In the amide 3, the free electron pair on the N atom is donated to the metal leading to a short Y–N bond which can be regarded as virtually a double bond. In the carbyl 4, the electron deficiency of the Y atom causes the formation of an "α-agostic Y···CH interaction". Due to these interactions the systems can be seen as effectively 16-electron systems. The remaining electron deficiency of the yttrium atom in both compounds is decreased by an additional intramolecular "γ-agostic Y···CH interaction" between the yttrium atom and the methyl groups of the amide or carbyl ligands, respectively, as can be clearly seen in the X-ray structure as well as in the solid-state ^{13}C NMR spectra.

Acknowledgment. This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

Registry No. 1, 40585-51-1; 2, 94348-90-0; 3, 102829-91-4; 4, 95197-83-4; Cp*H, 41539-64-4; $\mathrm{YCl_3{\cdot}3THF}$, 84147-94-4; $\mathrm{NaN(SiMe_3)_2}$, 1070-89-9; $\mathrm{LiCH(SiMe_3)_2}$, 41823-71-6.

Supplementary Material Available: Tables of positional and thermal parameters for all atoms and observed and calculated structure factors, a complete list of bond lengths and angles, and the ORTEP drawings of the three molecules (96 pages). Ordering information is given on any current masthead page.

Reactivity of Alkynes toward η^2-CX$_2$ (X = S, Se) Metal Complexes. 1. The [2 + 2] Condensation of an Alkyne on a Metal Carbene: An Experimental and Theoretical Study. 2. Formation and X-ray Structure of Unusual Doubly and Triply Condensed Cyclic Systems

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The reaction of $\mathrm{(triphos)RhCl(\eta^2\text{-}CX_2)}$ [X = S (1), X = Se (2); triphos = $\mathrm{CH_3C(CH_2PPh_2)_3}$] with $\mathrm{(CF_3)C{\equiv}C(CF_3)}$ leads to the formation of two new complexes of formula $\mathrm{(triphos)ClRhC(CF_3){=}C(CF_3)CXC(CF_3){=}C(CF_3)X}$ (3 and 4), containing a metallacyclobutene unit. The salient structural features of 3 have been ascertained by an X-ray structural study: hexagonal; $P6_1$; $a = 23.425\ (6)$ Å, $c = 18.982\ (5)$ Å; $R = 0.063$, $R_w = 0.060$ for 1334 reflections with $I \geq 3\sigma(I)$. A d^8-(triphos)RhCl fragment of the ML$_4$ type is linked to a chelating $\mathrm{C(CF_3){=}C(CF_3)CS_2C_2(CF_3)_2}$ ligand. The four-membered metallacyclobutene ring may result from the addition of an alkyne molecule to the Rh=C linkage of the carbenoid complex $\mathrm{(triphos)ClRh{=}CSC(CF_3){=}C(CF_3)S}$. By reaction with Ag$^+$ or Tl$^+$, Cl$^-$ is abstracted from 3 and 4 to give the products $\mathrm{[(triphos)RhC(CF_3){=}C(CF_3)CXC(CF_3){=}C(CF_3)X]BPh_4}$ (5 and 6). Eventually 3 and 4 can be regenerated from 5 and 6 by treatment with chloride anions. The crystal structure of 5 has been determined: monoclinic; $P2_1/a$; $a = 38.649\ (10)$ Å, $b = 12.281\ (4)$ Å, $c = 14.643\ (4)$ Å, $\beta = 97.64\ (2)°$; $R = 0.061$, $R_w = 0.061$ for 5294 reflections with $I \geq 3\sigma(I)$. With respect to 3, one sulfur atom of the five-membered 1,3-dithiol ring replaces the chloride ligand in the coordination of rhodium, thus restoring the original η^2-bonding mode of one C–S linkage as in the parent compounds 1. An unusual feature of 5 and 6 is that one three-, one four-, and one five-membered ring are all condensed and share an unique carbon atom. The problem of the addition of an alkyne to a M=C (metal–carbene) double bond is analyzed theoretically. Explanations are offered why this type of 2 + 2 cycloaddition, formally symmetry forbidden in organic chemistry, becomes allowed for organometallic reactions which lead to the formation of a metallacycle ring.

Introduction

The 1,3-dipole character of heteroallene molecules of the type X=C=Y (X, Y = S, NR) is enhanced by η^2-coordination to metal centers. Alkynes with electron-withdrawing substituents are known to react under mild conditions with η^2-CS$_2$[2] or η^2-SCNR (R = CH$_3$, C$_2$H$_5$)[3] metal complexes to give 1,3-dithiol-2-ylidene (A) or 1,3-thiazol-2-ylidene (B) derivatives, as shown in 1.

Both the dithiocarbenes of type A and the thiazacarbenes of type B have found useful applications in the synthesis of 1,3-dithiole-2-thiones[3] 1,3-thiazole-2-thiones[3] and substituted tetrathiafulvalenes.[2a–d,4]

With the aim of synthesizing new dithiocarbene deriv-

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[1] (a) ISSECC. (b) Cornell University.

[2] (a) Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486. (b) Le Marouille, J. Y.; Lelay, C.; Benoit, A.; Grandjean, D.; Touchard, D.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1980**, *191*, 133. (c) Bianchini, C.; Meli, A.; *J. Chem. Soc., Chem. Commun.* **1983**, 1309. (d) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1984**, *4*, 264. (e) Frazier, C. C.; Magnussen, N. D.; Osuji, L. N.; Parker, K. O. *Organometallics* **1982**, *1*, 903. (f) Schenk, W. A.; Scwietze, T.; Muller, H. *J. Organomet. Chem.* **1982**, *232*, C41.

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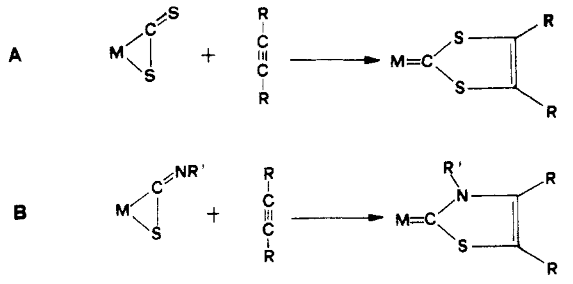
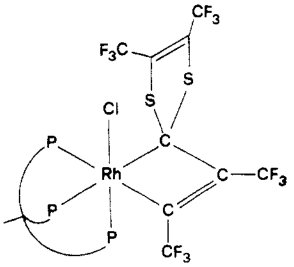


1

atives and also to check the behavior of the complexed η^2-CSe_2 molecule in analogous circumstances, we have treated (triphos)RhCl(η^2-CS_2)[5] (1) and (triphos)RhCl(η^2-CSe_2)[6] (2) [triphos = $CH_3C(CH_2PPh_2)_3$] with hexafluorobut-2-yne. Unexpectedly, both complexes add as



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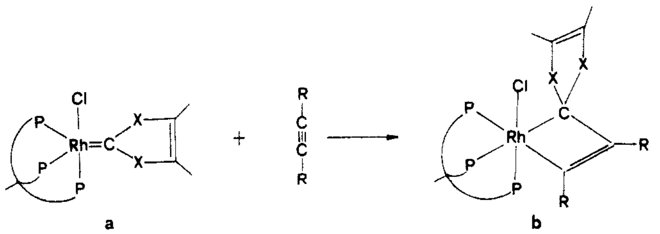
many as two molecules of alkyne to give the unprecedented rhodacyclobutene derivatives (triphos)ClRhC(CF_3)=C(CF_3)CXC(CF_3)=C(CF_3)X [X = S (3), X = Se (4)]. The crystal structure of 3 has been presented previously.[7] This complex, schematically shown in 2, is an uncommon example of a spiran-like organometallic molecule where two rings (a metallacyclobutene and a 1,3-dithio heterocycle) are joined through a shared carbon atom. Recently a related dimetalla spiro heterocycle has been reported as the product of the 3 + 2 cycloaddition of an imidoyl–cobalt unit and CS_2.[8]

Although we have no clear-cut experimental evidence, it may be safely assumed that the key intermediate in the reactions leading to 3 and 4 is a rhodium–carbene species which may add a second alkyne molecule as shown in 3.



3

In this paper we present in detail the chemistry and reactivity of the carbon disulfide and carbon diselenide derivatives 1 and 2. In addition, it will be shown that the chloride ligand can be easily abstracted from the products 3 and 4 to give new complexes with unique geometrical features.

The last section of the paper is devoted to a MO analysis of the formation of the rhodacyclobutene rings. There is a particular interest in doing so. Since the d^8-ML_4 unit (triphos)RhCl is isolobal with a methylene,[9] the reaction in 3 may be viewed as the equivalent of the addition of an acetylene to an olefin, that is a 2 + 2 addition. These reactions are well established to be symmetry-forbidden processes.[10] Even though the presence of the metal atom technically suppresses the symmetry-based barrier,[11] a substantial electronic barrier should remain. However, such reactions are often easily accessible thermally in organometallic chemistry; the metal-promoted metathesis of olefins[12] and alkynes[13,14] are two illustrative examples in which the key step is believed to involve this type of 2 + 2 addition. A number of recent papers[15-17] discuss in some details this apparently contradictory result.

Results and Discussion

Synthesis and Structural Characterization of the Complexes. Yellow crystals of 3 and 4 are formed in 90% yield by reacting at room temperature CH_2Cl_2 solutions of 1 and 2 with a twofold excess of $(F_3C)C{\equiv}C(CF_3)$. When stoichiometric amounts of alkyne are used, compounds 3 and 4 are obtained in ca. 40% yield, together with equal amounts of the starting η^2-heteroallene complex.

Compounds 3 and 4 are diamagnetic and air-stable in the solid state. They are insoluble in common organic solvents and thus have not been studied in solution. Their IR spectra in the region 4000–400 cm^{-1} are superimposable on each other. Medium absorption at 1625 and 1605 cm^{-1} are assigned to $\nu(C{=}C)$ of alkene moieties.[2d] A series of strong bands between 1300 and 1100 cm^{-1} (1270, 1240, 1170, and 1130 cm^{-1}) reveals the presence of CF_3 groups[2d] in both compounds. An Ortep drawing of the structure of 3 is presented in Figure 1.

There has been no substantial improvement on the refinement of the structure with respect to what previously reported[7] on account of the low number of measurable reflections. Accordingly only the salient features of the molecule will be illustrated. The geometry is pseudooctahedral about the rhodium atom. Notice that the chlorine atom is in a trans-axial position with respect to the atom P(3) [P(3)–Rh–Cl = 169.8 (3)°] and that the atoms P(1), P(2), C(6), and C(8) describe fairly well the equatorial plane (largest deviation from the least-squares plane = 0.1 Å). Perhaps the best way of looking at the molecule is by focusing on the metallacyclobutene ring. Two adjacent

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[11] This arises because the only element of symmetry maintained throughout the reaction path contains the broken and formed bonds.

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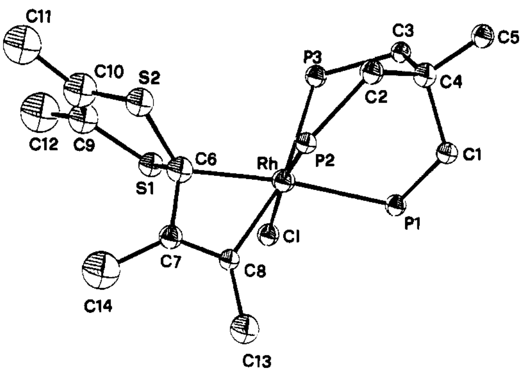


Figure 1. An Ortep drawing of the complex (triphos)ClRhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S (3).

Table I. Selected Bond Distances (Å) and Angles (deg) for Compound 3

	Bond Distances		
Rh-Cl	2.424 (9)	S(1)-C(9)	1.74 (4)
Rh-P(1)	2.446 (8)	S(2)-C(6)	1.86 (3)
Rh-P(2)	2.450 (9)	S(2)-C(10)	1.68 (4)
Rh-P(3)	2.306 (9)	C(6)-C(7)	1.50 (4)
Rh-C(6)	2.14 (3)	C(7)-C(8)	1.30 (4)
Rh-C(8)	2.05 (3)	C(9)-C(10)	1.38 (4)
S(1)-C(6)	1.84 (3)		
	Bond Angles		
Cl-Rh-P(1)	87.1 (3)	P(3)-Rh-C(6)	98 (1)
Cl-Rh-P(2)	100.4 (3)	P(3)-Rh-C(8)	90 (1)
Cl-Rh-P(3)	169.9 (3)	C(6)-Rh-C(8)	63 (1)
Cl-Rh-C(6)	85.7 (9)	C(7)-C(6)-Rh	90 (2)
Cl-Rh-C(8)	82.9 (9)	S(1)-C(6)-S(2)	104 (2)
P(1)-Rh-P(2)	82.4 (3)	C(7)-C(8)-Rh	102 (2)
P(1)-Rh-P(3)	88.7 (3)	C(6)-C(7)-C(8)	103 (3)
P(2)-Rh-P(3)	88.4 (3)	S(1)-C(9)-C(10)	113 (3)
P(1)-Rh-C(6)	172 (1)	S(2)-C(10)-C(9)	120 (3)
P(1)-Rh-C(8)	113 (1)	C(6)-S(1)-C(9)	100 (2)
P(2)-Rh-C(6)	101 (1)	C(7)-S(2)-C(10)	99 (2)
P(2)-Rh-C(8)	164 (1)		

methylene residues have been substituted for by a d^8-ML_4 fragment, (triphos)RhCl, and a five-membered 1,3-dithioheterocycle. The four-membered metallacycle is substantially planar (the largest deviation from the least-squares plane is ca. 0.01 Å). Also, the two condensed rings are almost perpendicular to each other (dihedral angle between the planes ca. 88°). In spite of the large standard deviations which affect the bond distances (Table I), there is sufficient indication that the C(7)–C(8) and the C(9)–C(10) linkages have the expected double-bond character.

Metathetical reactions of 3 and 4 with a variety of anions such as BPh_4^-, PF_6^-, BF_4^-, Br^-, and I^- did not lead to the replacement of the chloride ion in 3 and 4. This is indirect chemical evidence that Cl^- is bound to the metal in both compounds. By contrast, the chloride ion is easily abstracted by Ag^+ or Tl^+ to give red cationic derivatives, which have been isolated as BPh_4^- salts. The latter have general formula [(triphos)RhC(CF_3)=C(CF_3)CXC(CF_3)=C(CF_3)X]BPh_4 [X = S (5), X = Se (6)].

Compounds 5 and 6 are diamagnetic and air-stable in the solid state and in solution as well. They are soluble in common organic solvents, in which they behave as 1:1 electrolytes (molar conductance value in 10^{-3} M nitroethane solution: 43 Ω cm^2 mol^{-1} for 5; 45 Ω cm^2 mol^{-1} for 6). The IR spectra are superimposable on each other and show two ν(C=C) stretching vibrations at 1605 and 1585 cm^{-1}. Bands at 1295, 1280, 1265, 1240, 1180, 1140, and 1120 cm^{-1} are assigned to CF_3 groups. The $^{31}P\{^1H\}$ NMR spectra of 5 and 6 (CD_2Cl_2, −60 °C) exhibit a typical ABCX pattern. The presence of three types of phosphorus atoms is revealed, giving resonances in a 1:1:1 ratio, each split by the rhodium nucleus. An Ortep drawing of the complex cation in 5 is shown in Figure 2.

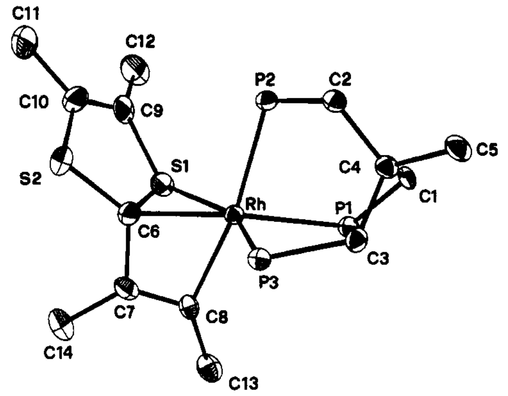


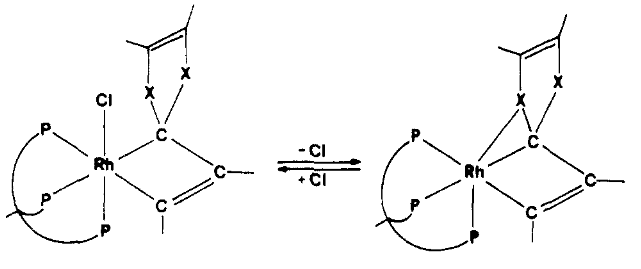
Figure 2. An Ortep drawing of the complex cation [(triphos)RhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S]$^+$ (5).

Table II. Selected Bond Distances (Å) and Angles (deg) for Compound 5

	Bond Distances		
Rh-S(1)	2.426 (3)	S(2)-C(10)	1.72 (1)
Rh-P(1)	2.402 (2)	C(6)-C(7)	1.50 (1)
Rh-P(2)	2.386 (2)	C(7)-C(8)	1.33 (1)
Rh-P(3)	2.340 (3)	C(8)-C(13)	1.49 (1)
Rh-C(6)	2.115 (9)	C(7)-C(14)	1.50 (2)
Rh-C(8)	2.137 (9)	C(9)-C(10)	1.37 (2)
S(1)-C(6)	1.81 (1)	C(9)-C(12)	1.51 (2)
S(1)-C(9)	1.75 (1)	C(10)-C(11)	1.51 (2)
S(2)-C(6)	1.77 (1)		
	Bond Angles		
S(1)-Rh-P(1)	116.2 (1)	P(3)-Rh-C(8)	91.9 (3)
S(1)-Rh-P(2)	98.5 (1)	C(6)-Rh-C(8)	63.9 (4)
S(1)-Rh-P(3)	152.6 (1)	C(7)-C(6)-Rh	92.5 (6)
S(1)-Rh-C(6)	46.3 (3)	S(1)-C(6)-S(2)	115.5 (5)
S(1)-Rh-C(8)	76.0 (3)	C(7)-C(8)-Rh	96.7 (6)
P(1)-Rh-P(2)	85.3 (1)	C(6)-C(7)-C(8)	104.8 (8)
P(1)-Rh-P(3)	90.5 (1)	S(1)-C(9)-C(10)	115.0 (9)
P(2)-Rh-P(3)	89.2 (1)	S(2)-C(10)-C(9)	119.3 (9)
P(1)-Rh-C(6)	159.6 (3)	C(6)-S(1)-C(9)	96.3 (5)
P(1)-Rh-C(8)	104.9 (3)	C(7)-S(2)-C(10)	96.5 (5)
P(2)-Rh-C(6)	106.0 (3)	S(1)-C(9)-C(12)	117.0 (9)
P(2)-Rh-C(8)	169.7 (3)	S(2)-C(10)-C(11)	115.0 (9)
P(3)-Rh-C(6)	106.3 (3)		

The relevant bond distances and angles are listed in Table II. The abstraction of one chloride ion from 3 has not induced the rupture of the metallacyclobutene ring, although some major geometrical rearrangements have occurred. The latter are driven by the necessity of bringing into the coordination sphere one of the sulfur atoms of the 1,3-dithio heterocycle to replace the abstracted chloride. Still the complex can be described as pseudooctahedral if one consider the atoms C(6) and S(1), bonded to each other, as two distinct ligands. Actually, the attainment of the η^2-coordination mode of one C–S linkage and the formation of the three-membered cycle is one of the most remarkable features of the complex. There are now three condensed cycles (three-, four-, and five-membered) which share one carbon atom, C(6). There may be some strain in attaining this unusual molecular conformation, as shown by the imperfect planarity of the four-membered metallaring (the deviations from the least-squares plane can be as large as 0.10 (7) Å). If we compare the relative orientations of the four- and five-membered cycles and that of the (triphos)Rh fragment, we notice some major rearrangements with respect to the previous structure. The plane of the metallacyclobutene ring is no longer coplanar with one of the RhP_2 planes but is rotated by 82° so that the C(8) atom now occupies one axial position. Also, notice that the 1,3-dithio heterocycle is no longer perpendicular to the metallacyclobutene ring (dihedral angle between the planes 66.6°). Finally the five- and three-membered rings are far from being coplanar (dihedral angle between the planes ca. 125.7°). This feature suggests that the sulfur atom is roughly sp^3 hybridized and that the coordinating lone pair, replacing that of chloride, has prevalent out-of-plane p orbital character.

Interestingly **5** and **6** can be easily converted into the parent compounds **3** and **4** by addition of chloride anions (from PPNCl salt) to their solutions; see 4.



4

MO Analysis. Formation of the Metallacyclobutene. The key step for the formation of the metallacycle seems to be reaction 3: a d^8-Rh–carbene complex, **3a**, adds an alkyne across the metal–carbon double bond to generate the corresponding metallacyclobutene **3b**.

A good starting point for the investigation of 3 is the electronic structure of the reactant, the metal–carbene **3a**. The formation of the latter from the Rh–η^2-CS_2 complex and alkyne is discussed elsewhere[18] as a part of a general study of the reactivity patterns in metal–CS_2 systems. Here it is sufficient to have in hand the molecular orbitals of the d^8-ML_4–carbene complex. These can be constructed by using the familiar fragmentation approach[19] from those of a C_{2v}-ML_4 unit (a simple d^8-RhH_4^{3-} model has been used) and those of the 1,3-dithiol-2-ylidene fragment which has the features of a carbenic fragment. The process is carried out in Figure 3.

At the left are the MOs of the metallic unit. The pattern has been derived in some detail by others,[20] and only the salient features need to be repeated here. Take the 3-below-2 splitting of an octahedral ML_6 system and remove two cis ligands from it. The e_g set is split considerably; the d_{x^2} orbital ($3a_1$) is practically unperturbed whereas the d_{yz} orbital (b_2) mixes in some p_z character and drops in energy (note the unorthodox coordinate system, which is required for subsequent study of the reactivity of the carbene). Also a metal sp hybrid, $2a_1$, descends to low energy. The t_{2g} set emerges rather unperturbed as a triad of a_2, b_1, and $1a_1$ orbitals. Only the levels through b_2 are filled in this d^8 fragment.

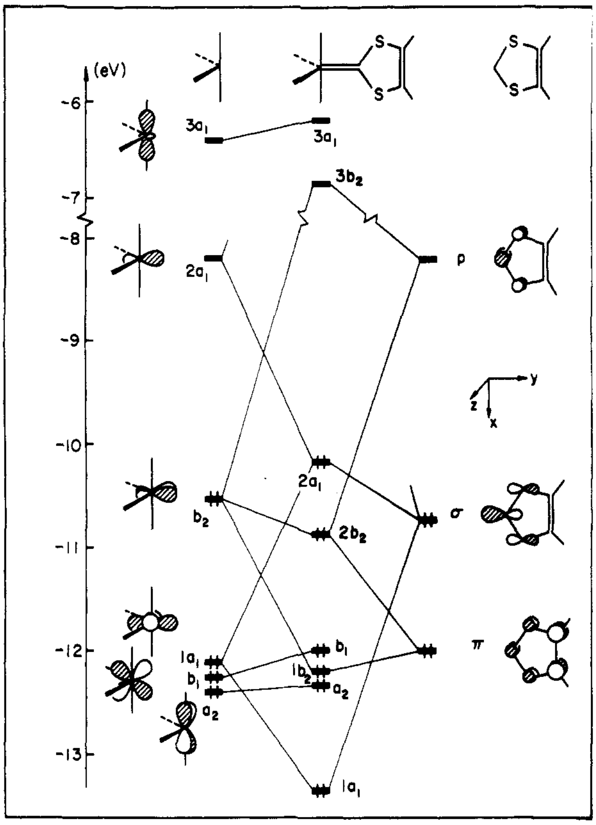


Figure 3. Diagram for the interaction between a d^8-ML_4 fragment and a 1,3-dithio heterocycle.

At right in Figure 3 are the valence orbitals of the five-membered ring. One recognizes the LUMO and HOMO centered on the carbon atom and consisting primarily of a p orbital and a σ lone pair, respectively, both typical of a carbene species. Also, the latter orbitals are substantially similar in energy and shape to the typical a_1 and b_2 π^*-levels of a bent CS_2 molecule,[21-23] irrespective of the fact that the CS_2 unit here is a part of the cycle. The LUMO may also be viewed as the fourth π-orbital of the five-membered-ring π-framework. Below the HOMO (labeled σ) one finds a π-type orbital localized on the two carbon atoms and accounting for the carbon–carbon double bond. Not shown, and buried lower in energy, are the fully π-bonding levels of the ring and the two symmetry combinations of the sulfur σ lone pairs.

Interacting the two subsets of fragment orbitals produces the pattern displayed in the middle of Figure 3. The σ-donor orbital of the carbene interacts with both orbitals of a_1 symmetry to produce $1a_1$, fully bonding between the metal and carbon atom (this is the Rh–C σ-bond), $2a_1$, and the high-lying $3a_1$. Similarly b_2 interacts primarily with p producing a substantial amount of back-donation. One should notice, however, that π mixes into $2b_2$ and mitigates somewhat the strength of this interaction. This destabilizing effect would be larger if the cycle were rotated by 90°, since b_1 and not b_2 would match π and p in symmetry. This argument lies at the heart of the preferred orientation of CR_2 units in metal–carbene complexes.[24]

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A comment relative to the $\sigma - p$ splitting on the right of Figure 3 is in order here. In the frozen geometry used,[25] the numerical results lead us to believe that the carbene is in a singlet state configuration. From an orbital point of view, the reason is that the LUMO (p) is C–S π-antibonding, hence destabilized with respect to a pure p carbon atomic function. Also the σ-orbital is stabilized as the S–C–S angle is closed, as is typical for in-plane π^*-orbital of AB_2 molecules when they are bent. Here the angle used for the calculations is as small as 110°. We face, however, the problem of understanding the observed formation of tetrathiofulvalene derivatives[2d] which can result allegedly from the coupling of two triplets.[26] Assuming no intersystem crossing,[27] the carbenoid 1,3-dithiol-2-ylidene ring is then generated as a triplet. This situation could arise, as suggested by Hall and Taylor.[28] It could be that the geometry of the cycle within the organometallic system is different from that of the cycle in the gas phase. Notice that the transfer of one electron from σ to π, as it would occur in the triplet state, is consistent with a larger S–C–S angle and longer C–S distances. In turn, the triplet state becomes energetically more accessible than would be anticipated only on the basis of the $\sigma - p$ splitting given in Figure 3.

In looking for possible paths to generate the metallacyclobutene **3b**, one faces the choice between two routes: (i) prior coordination of the alkyne and collapse into the four-membered ring; (ii) direct cycloaddition. One quickly realizes that the first possibility involves a high-energy 20e species, unlikely to be formed under the experimental conditions of the reaction. We decided therefore to investigate a direct addition using an idealized one-dimensional potential surface; in other words, all the bond-breaking and -forming processes occur simultaneously, in a synchronized manner. We start with an acetylene at infinite distance and slowly bring it across the Rh=C double bond, eventually forming the metallacyclobutene **3b**. This is an assumed and reasonable transit, not a complete potential energy surface.

Due to the low symmetry of the overall system (only a mirror plane of symmetry is maintained throughout, that containing the incipient metallacyclobutene), disentangling the Walsh diagram turns out to be a relatively complex task. We may however simplify the analysis and concentrate on those orbitals symmetric with respect to the mirror plane. After all, the action takes place in this plane; bonds are formed and broken in this region of space. Figure 4 displays the evolution of these MOs as a function of the reaction coordinate.

At the left-hand side are $1b_2$, $2b_2$, $2a_1$, $3b_2$, and $3a_1$ of Figure 3. In between and boxed with a dashed line, we have inserted the in-plane acetylene π-orbital (π_σ) and its antibonding counterpart (π_σ*). Recall that the pattern is at this point a bare superposition of the levels of the trigonal-bipyramidal carbene with the two relevant levels of an acetylene.[29]

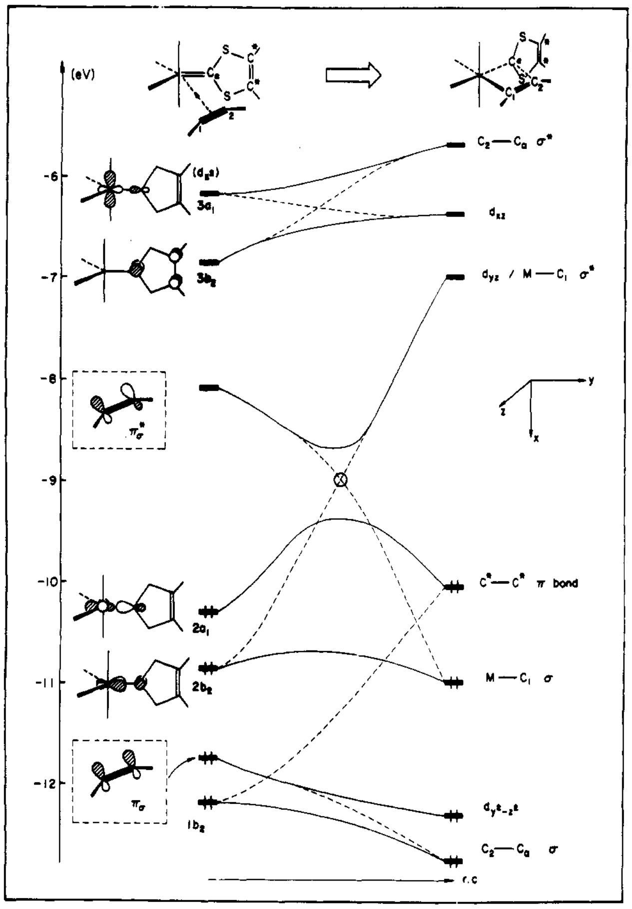
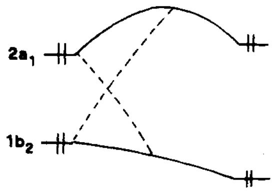


Figure 4. Evolution of the MO's for the formation of the metallacyclobutene system.

When the acetylene is brought in toward the metal complex, all orbitals mix with each other. The actual connections between the starting and ending point of the reaction are drawn with solid lines. However, we wish to understand the intended correlations and those are represented by the dashed lines. What matters in this case in the composition or the character of each molecular orbital. For example, let us take $2b_2$. Technically it correlates with the newly formed Rh–C σ-bond. Yet, this orbital is d_{yz} in character and should evolve as one component of the pseudo e_g set of the octahedral pattern, i.e., high lying and empty. Similarly, $2a_1$ is mainly $d_{y^2-z^2}$ and should emerge as basically nonbonding, down in energy as one component of the pseudo t_{2g} set. The whole picture of Figure 4 may be analyzed along these lines.

Why the molecular orbitals behave the way they do? Simple and qualitative perturbation theory arguments[30] help to answer the question. The Walsh diagram of Figure 4 may be easily decomposed into two subsets. The first one involves $1b_2$ and $2a_1$. The latter is stabilized by the geometrical distortion (loss of Rh–C σ-antibonding) while the former tends to be destabilized by the loss of Rh–C π-bonding. These "intended" behaviors are shown in **5** with dashed lines.



5

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(25) That of the cycle found by P. H. Dixneuf and co-workers in: Le Bozec, H.; Dixneuf, P. H.; Adams, R. D. *Organometallics* **1984**, *3*, 1919.

(26) Two singlet methylenes face a high energy barrier if approached along a least-motion path. Dimerization of the singlets can be however attained through a non-least-motion path so that a σ lone pair of one impinges on the π system of the other. See: Hoffmann, R.; Gleiter, R.; Mallory, F. B. *J. Am. Chem. Soc.* **1970**, *92*, 1460. Also, see ref 21 and references therein.

(27) Dimerization of carbenes via an "interystem crossing" cannot be definitely excluded as shown by: Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

(28) Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1576.

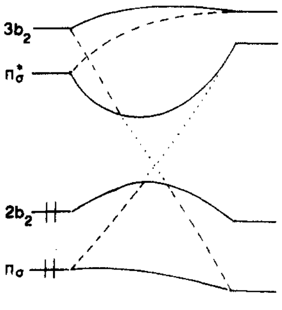
(29) The two MO's descend from the in-plane π and π^* orbitals but are hybridized upon bending of hydrogens away from the metal; see: Hoffman, D. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

Now recall that $2a_1$ and $1b_2$ are of the same symmetry in our C_s system: they repel each other. Essentially, $1b_2$ mixes in an antibonding way into $2a_1$, pushing it upwards. And $2a_1$ mixes in a bonding manner into $1b_2$, stabilizing it, solid line in **5**. A strongly avoided crossing takes place.

The second type of interaction drives the $2\pi + 2\pi$ cycloaddition and features π_σ, $2b_2$, π_σ^*, and $3b_2$.

Molecular orbitals π_σ and $2b_2$ undergo a 4e/2-orbital destabilizing interaction. As a result π_σ is pushed down whereas $2b_2$ should be destabilized. Technically, this destabilization is added to that of $2a_1$ which is of the same symmetry and higher in energy. Conversely, π_σ^* and $3b_2$ enter a 0e/2-orbital interaction pattern that stabilizes tremendously π_σ^* which eventually maintains $2b_2$ (or rather $2a_1$, vide supra) low in energy via the circled avoided crossing. The latter is absent in the case of a "pure" $2\pi + 2\pi$ addition in organic chemistry so that the reaction is indeed symmetry-forbidden.

A pictorial summary of the above considerations is shown in **6**. The dashed lines stand for the 2-orbital interactions, whereas the crossing between the dotted lines is the one which is present in organic systems but absent in the present case. One realizes that there should be an electronically induced barrier for the process: $2b_2$ (in fact $2a_1$, see above) is substantially destabilized at the transition state.



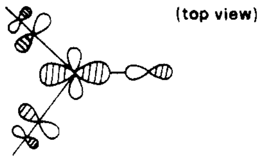
6

However the reaction is a facile process and our computation shows no barrier at all for the reaction. This probably is an artifact of the method used in this work but still leads us to think that the barrier, if any, is a small one. Essentially the activation energy is the difference between the destabilization of $2b_2$ (or rather $2a_1$ here) and the stabilization of π_σ. The molecular orbital $2a_1$ starts relatively high in energy, since it is metal–carbon σ-antibonding. In turn, that means that it does not have to rise too much in energy before it gets depressed in energy by π_σ^*. Essentially the metal d-centered $2a_1$ acts as a buffer between $2b_2$ and π_σ^*. Electronically the process is reminiscent of the situation encountered in the Tebbe reaction[31] taking $Cp_2Ti(CH_2)(C_2H_2)$ into a metallacyclobutene. The electronic features of the reaction have been discussed elsewhere.[15a,32] We only point out that in both cases a metal orbital ($2a_1$ in Figure 4) acts as a mediator via an oxidation of the metal center along the reaction.

Returning to Figure 4, one would anticipate that the higher $2a_1$ and the lower π_σ^*, the smaller the activation energy should be. The relative position of $2a_1$ and $2b_2$ should be primarily a function of the substituents. It is therefore not surprising to find strong acceptors on the acetylene [R = CF_3 in **3** and **4**)[33] and no π acceptor on Rh. For example, carbonyl ligands on Rh would push $2a_1$ down in energy via interaction of type **7** between $d_{y^2-z^2}$ and CO π^*'s.

Table III. Summary of Crystal Data

	3	5
formula	$C_{50}H_{39}ClF_{12}P_3S_2Rh$	$C_{74}H_{59}BF_{12}P_3S_2Rh\cdot CH_2Cl_2$
mol wt	1163.26	1531.97
cryst form	hexagonal needle	parallelepiped
cryst size, mm	0.09 × 0.09 × 0.55	0.08 × 0.32 × 0.35
space group	$P6_1$	$P2_1/a$
a, Å	23.425 (6)	38.649 (10)
b, Å	23.425 (6)	12.281 (4)
c, Å	18.982 (5)	14.643 (4)
β, deg		97.64 (2)
V, Å^3	9020.5	6888.6
Z	6	4
d_{calcd}, g cm^{-3}	1.28	1.48
μ(Mo Kα), cm^{-1}	5.3	5.2
radiatn	graphite-monochromated Mo Kα (λ = 0.71069 Å)	
2θ range, deg	5–50	5–50
scan width, deg	0.08	0.9
scan speed, deg s^{-1}	0.04	0.05
total data	5898	13229
unique data, $I \geq 3\sigma(I)$	1334	5294
no. of parameters	236	296
R	0.063	0.061
R_w	0.060	0.061



7

Considerations on the Formation and Electronic Structure of the Cations [(triphos)$\overline{\text{RhC}(CF_3)=\text{C}(CF_3)\text{CXC}(CF_3)=\text{C}(CF_3)\text{X}}$]$^+$.

There is little doubt that the forced removal of chloride from the coordination sphere generates an electron deficiency on the metal. Eventually, this "hole" may be filled by one sulfur lone pair. The X-ray study of **5** shows that this is geometrically feasible with some appropriate reorientations of the four- and five-membered rings relative to the (triphos)Rh fragment. Ultimately, one of the two C–S linkages is η^2-coordinated to the metal, a reminder of the η^2-coordination of the parent Rh–η^2-CS_2 complex **1**.

However, the bonding in **5** is substantially different from that in **1**. It was pointed out elsewhere[21] that the η^2-bonding of a CS_2 species to a metal atom ranges between two limiting descriptions, namely, the Dewar–Chatt–Duncanson (DCD) and the metallacyclopropane models. Essentially, the difference is all in the assignment for the two pairs of electrons forming the M–S and M–C bonds.

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(30) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(31) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5585.

(32) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chim.* **1983**, *7*, 535.

(33) The formation of complexes of type **3** and **4** is also possible with other electrophilic alkynes bearing electron-withdrawing substituents on both sides (e.g., $MeO_2CC{\equiv}CCO_2Me$). When monosubstituted alkynes are used (e.g., $HCC{\equiv}CCO_2Me$), the reactions with **1** and **2** give the known μ-C_2X_4 dimeric complexes [(triphos)Rh(μ-C_2X_4)Rh(triphos)]$^{2+}$ (X = S, Se).[5,6]

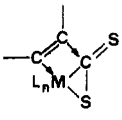
Table IV. Final Atomic Parameters for Compound 3[a]

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
Rh	5978 (1)	4676 (1)	0	33 (2) (U_{eq})	C14	6501 (24)	6339 (20)	−1245 (25)	96 (16)
Cl	6615 (4)	4488 (4)	−881 (5)	46 (3)	C1 1	5600 (8)	2929 (11)	137 (12)	47 (10)
S1	7499 (4)	5902 (4)	−408 (5)	47 (3)	C2 1	5171 (8)	2297 (11)	392 (12)	50 (11)
S2	6783 (5)	6325 (5)	516 (6)	54 (3)	C3 1	5394 (8)	1851 (11)	487 (12)	48 (10)
P1	5251 (4)	3480 (4)	35 (6)	35 (2)	C4 1	6046 (8)	2036 (11)	329 (12)	55 (11)
P2	6421 (4)	4463 (4)	1074 (5)	36 (3)	C5 1	6474 (8)	2667 (11)	74 (12)	50 (10)
P3	5227 (4)	4783 (4)	691 (5)	30 (2)	C6 1	6252 (8)	3114 (11)	−22 (12)	64 (11)
F1	7474 (18)	7501 (17)	1278 (21)	77 (12)	C1 2	4687 (11)	3001 (11)	−697 (10)	43 (10)
F1*	8272 (29)	7996 (25)	423 (32)	58 (16)	C2 2	4004 (11)	2627 (11)	−618 (10)	56 (11)
F2	8516 (27)	7831 (27)	951 (34)	130 (20)	C3 2	3610 (11)	2278 (11)	−1190 (10)	68 (12)
F2*	7388 (35)	7743 (34)	669 (43)	116 (24)	C4 2	3898 (11)	2303 (11)	−1841 (10)	32 (9)
F3	7841 (25)	7995 (20)	212 (24)	96 (14)	C5 2	4581 (11)	2678 (11)	−1920 (10)	58 (11)
F3*	8174 (37)	7627 (31)	1257 (38)	93 (23)	C6 2	4975 (11)	3027 (11)	−1347 (10)	38 (10)
F4	8996 (30)	7191 (35)	345 (37)	168 (26)	C1 3	7075 (10)	4243 (8)	1036 (10)	19 (8)
F4*	8951 (21)	6778 (21)	−248 (29)	46 (13)	C2 3	7581 (10)	4530 (8)	540 (10)	29 (9)
F5	8830 (21)	7709 (23)	−512 (27)	99 (14)	C3 3	8096 (10)	4393 (8)	556 (10)	46 (10)
F5*	9029 (36)	7598 (41)	115 (50)	123 (27)	C4 3	8105 (10)	3970 (8)	1067 (10)	31 (9)
F6	8773 (21)	6794 (22)	−843 (27)	107 (15)	C5 3	7598 (10)	3683 (8)	1563 (10)	54 (10)
F6*	8613 (34)	7209 (42)	−894 (46)	123 (26)	C6 3	7083 (10)	3820 (8)	1547 (10)	33 (9)
F7	4999 (9)	4248 (9)	−1602 (12)	68 (6)	C1 4	6827 (11)	5131 (11)	1730 (10)	44 (10)
F8	5581 (10)	5178 (10)	−2062 (12)	76 (7)	C2 4	7425 (11)	5676 (11)	1529 (10)	50 (10)
F9	4807 (10)	5039 (10)	−1365 (11)	72 (7)	C3 4	7774 (11)	6190 (11)	2003 (10)	74 (13)
F10	5963 (11)	6364 (10)	−1460 (11)	83 (7)	C4 4	7525 (11)	6160 (11)	2678 (10)	70 (12)
F11	6793 (13)	6294 (12)	−1824 (15)	120 (10)	C5 4	6927 (11)	5615 (11)	2879 (10)	87 (14)
F12	6933 (13)	6869 (13)	−964 (14)	116 (9)	C6 4	6579 (11)	5101 (11)	2405 (10)	40 (10)
C1	4704 (16)	3284 (16)	839 (14)	53 (11)	C1 5	4396 (11)	4461 (11)	348 (11)	32 (9)
C2	5768 (11)	3767 (13)	1586 (19)	37 (9)	C2 5	4167 (11)	4067 (11)	−253 (11)	53 (11)
C3	5055 (14)	4322 (11)	1528 (17)	34 (9)	C3 5	3506 (11)	3781 (11)	−446 (11)	64 (12)
C4	5070 (11)	3674 (11)	1506 (13)	36 (9)	C4 5	3073 (11)	3889 (11)	−39 (11)	69 (12)
C5	4633 (15)	3256 (15)	2120 (15)	42 (10)	C5 5	3302 (11)	4283 (11)	563 (11)	50 (10)
C6	6656 (16)	5700 (16)	−164 (19)	50 (10)	C6 5	3964 (11)	4569 (11)	756 (11)	52 (11)
C7	6262 (15)	5723 (15)	−775 (18)	38 (10)	C1 6	5387 (9)	5600 (10)	967 (11)	31 (9)
C8	5782 (15)	5115 (16)	−827 (16)	45 (10)	C2 6	5647 (9)	5858 (10)	1629 (11)	39 (9)
C9	7945 (18)	6704 (17)	−83 (22)	65 (11)	C3 6	5811 (9)	6502 (10)	1798 (11)	71 (12)
C10	7582 (21)	6872 (19)	355 (23)	84 (14)	C4 6	5714 (9)	6887 (10)	1305 (11)	51 (11)
C11	7805 (28)	7534 (22)	728 (31)	99 (17)	C5 6	5454 (9)	6629 (10)	644 (11)	67 (13)
C12	8685 (21)	7130 (30)	−252 (39)	122 (21)	C6 6	5290 (9)	5985 (10)	475 (11)	39 (9)
C13	5279 (17)	4890 (18)	−1431 (17)	57 (12)					

[a] Coordinates multiplied by 10^4 and temperature factors by 10^3. Asterisks denote alternative positions of the disordered F atoms refined with occupancy factors 0.4.

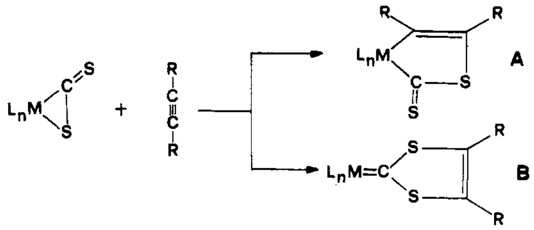
The metal–olefin description (DCD model) assigns two electrons to the metal (those participating in the π-back-donation) whereas the other two electrons are those of the π-bond of the coordinated linkage (notice that in CS_2 the π-bond is actually delocalized over the three centers).[23] Conversely if all of the four electrons belong formally to the ligand, another bonding description becomes more realistic; both the carbon and the sulfur atoms carry one lone pair for donation and there is no residual π-bond between these atoms. In **5** both the chemical and structural information agree for a description of the Rh–η^2-CS bonding according to this second model. The plane of the CS_2 grouping is neither coplanar nor perpendicular to that of the three-membered ring Rh–C–S, thus excluding interactions with any kind of C–S π-bond. Also, the distance of 1.81 (1) Å, the longest found for η^2-coordinated C–S, is exactly what would be expected for a single C–S bond. This is the value reported for the molecule $(CH_3)_2S$.[34] Thus in this case we may be at one end of the spectrum ranging between the two models of CS_2 coordination.

As a final remark, we would like to address the question as to whether direct addition of an alkyne across the M–C linkage of a M–η^2-CS_2 framework is chemically possible, while both the M–S and M–C bonds are retained (see **8**).



8

The experimental evidence[23] shows that the addition of an alkyne to M–η^2-CS_2 complexes usually cleaves the M–S bond and yields five-membered cycles of either type **9A** or **9B**.



9

It may be, however, that an attack of type **8** could be induced by the appropriate substitution at the exocyclic sulfur atom or by transforming the nature of the metal fragment. A possible strategy is to force some dipole character on the M–C linkage in order to add the alkyne (dipolarophile). A residual positive charge on the carbon atom can be obtained by alkylating the exocyclic sulfur atom. However, the resulting system can be described with three resonance structures **10a–c**, of which **10b** is certainly

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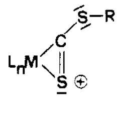
(34) Maier, W. *Angew. Chem.* **1961**, *73*, 120.

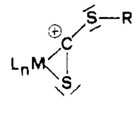
Table V. Final Positional Parameters ($\times 10^4$) for Compound 5[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Rh	1512.6 (2)	523 (1)	7707 (1)	C6 3	907 (1)	−988 (5)	4890 (4)
P1	1082 (1)	1741 (2)	6941 (2)	C1 4	1373 (2)	−2267 (5)	6756 (4)
P2	1222 (1)	−846 (2)	6735 (2)	C2 4	1337 (2)	−2931 (5)	7510 (4)
P3	1147 (1)	125 (2)	8815 (2)	C3 4	1431 (2)	−4027 (5)	7498 (4)
S1	2071 (1)	484 (2)	7125 (2)	C4 4	1562 (2)	−4458 (5)	6732 (4)
S2	2183 (1)	−1461 (2)	8318 (2)	C5 4	1598 (2)	−3793 (5)	5978 (4)
C1	666 (2)	1014 (7)	6630 (6)	C6 4	1504 (2)	−2698 (5)	5990 (4)
C2	769 (2)	−1008 (7)	6979 (6)	C1 5	1186 (1)	867 (5)	9923 (4)
C3	690 (2)	344 (7)	8296 (6)	C2 5	910 (1)	1470 (5)	10189 (4)
C4	595 (2)	56 (7)	7253 (6)	C3 5	947 (1)	1986 (5)	11045 (4)
C5	195 (2)	−150 (8)	7133 (7)	C4 5	1261 (1)	1899 (5)	11635 (4)
C6	2008 (2)	−127 (8)	8213 (6)	C5 5	1536 (1)	1296 (5)	11370 (4)
C7	2084 (3)	775 (8)	8903 (6)	C6 5	1499 (1)	780 (5)	10514 (4)
C8	1841 (2)	1526 (8)	8650 (6)	C1 6	1171 (1)	−1269 (5)	9269 (4)
C9	2203 (2)	−710 (10)	6613 (7)	C2 6	873 (1)	−1898 (5)	9309 (4)
C10	2271 (3)	−1574 (10)	7199 (8)	C3 6	903 (1)	−2938 (5)	9694 (4)
C11	2452 (4)	−2614 (16)	6991 (13)	C4 6	1230 (1)	−3349 (5)	10040 (4)
C12	2302 (3)	−602 (16)	5654 (9)	C5 6	1529 (1)	−2720 (5)	10000 (4)
C13	1871 (3)	2699 (9)	8918 (8)	C6 6	1499 (1)	−1680 (5)	9615 (4)
C14	2399 (3)	735 (11)	9618 (8)	C1 7	425 (2)	4966 (5)	2147 (3)
F1	1726 (2)	3346 (4)	8250 (4)	C2 7	312 (2)	4172 (5)	2723 (3)
F2	1727 (2)	2943 (5)	9675 (4)	C3 7	144 (2)	3239 (5)	2344 (3)
F3	2206 (2)	3026 (5)	9075 (5)	C4 7	88 (2)	3100 (5)	1391 (3)
F4	2693 (2)	832 (9)	9256 (6)	C5 7	201 (2)	3893 (5)	815 (3)
F5	2400 (2)	1485 (7)	10272 (5)	C6 7	369 (2)	4826 (5)	1193 (3)
F6	2418 (2)	−209 (7)	10059 (5)	C1 8	541 (1)	6307 (5)	3660 (4)
F7	2104 (2)	−1214 (7)	5049 (5)	C2 8	726 (1)	5819 (5)	4436 (4)
F8	2271 (2)	425 (9)	5372 (5)	C3 8	622 (1)	5981 (5)	5302 (4)
F9	2633 (2)	−913 (9)	5626 (5)	C4 8	332 (1)	6631 (5)	5392 (4)
F10	2381 (3)	−3406 (7)	7538 (8)	C5 8	147 (1)	7118 (5)	4616 (4)
F11	2381 (2)	−2945 (8)	6132 (7)	C6 8	251 (1)	6956 (5)	3750 (4)
F12	2797 (2)	−2467 (8)	7156 (7)	C1 9	1081 (2)	5773 (5)	2661 (4)
B	656 (3)	6051 (9)	2597 (7)	C2 9	1321 (2)	6372 (5)	3255 (4)
C1 1	1192 (1)	2347 (5)	5880 (4)	C3 9	1678 (2)	6193 (5)	3266 (4)
C2 1	953 (1)	2459 (5)	5085 (4)	C4 9	1794 (2)	5416 (5)	2683 (4)
C3 1	1053 (1)	2966 (5)	4308 (4)	C5 9	1554 (2)	4817 (5)	2088 (4)
C4 1	1392 (1)	3362 (5)	4328 (4)	C6 9	61197 (2)	4996 (5)	2078 (4)
C5 1	1631 (1)	3251 (5)	5124 (4)	C110	556 (1)	7171 (5)	1920 (4)
C6 1	1532 (1)	2743 (5)	5900 (4)	C210	806 (1)	7975 (5)	1859 (4)
C1 2	919 (2)	2929 (5)	7524 (3)	C310	715 (1)	8933 (5)	1373 (4)
C2 2	685 (2)	3623 (5)	6999 (3)	C410	374 (1)	9086 (5)	948 (4)
C3 2	523 (2)	4460 (5)	7426 (3)	C510	123 (1)	8281 (5)	1010 (4)
C4 2	595 (2)	4604 (5)	8378 (3)	C610	214 (1)	7324 (5)	1496 (4)
C5 2	828 (2)	3910 (5)	8902 (3)	Cl1	2487 (3)	2986 (9)	6767 (7)
C6 2	990 (2)	3073 (5)	8475 (3)	Cl1A	2423 (4)	3751 (13)	6873 (10)
C1 3	1177 (1)	−528 (5)	5494 (4)	Cl2	3129 (4)	4029 (12)	7440 (10)
C2 3	1422 (1)	140 (5)	5154 (4)	Cl2A	3047 (4)	3642 (13)	8064 (11)
C3 3	1398 (1)	346 (5)	4211 (4)	C15	2767 (8)	3143 (24)	7658 (20)
C4 3	1128 (1)	−116 (5)	3607 (4)	C15A	2752 (16)	4541 (47)	7505 (39)
C5 3	882 (1)	−782 (5)	3947 (4)				

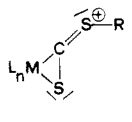
[a] Atoms labeled A belong to an alternative orientation of the disordered solvent molecule (population parameter 0.5).



10a



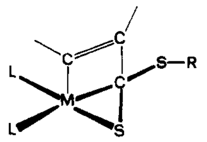
10b



10c

relevant but not necessarily predominant. All the M–η^2-SCSR moieties observed in X-ray crystallographic structure determinations are planar.[23] In MO terms this means that the carbon p_π orbital, which should be empty in order to react with the negative carbon of the incoming alkyne, is actually involved to a certain extent in π-interactions with the adjacent sulfur atoms.

The second requirement is that of an electron-rich metal. A d^8-ML_4 fragment where one of the ligands is a hydrogen, which can eventually be abstracted as a proton, should be adequate. As an alternative the starting M–η^2-CS_2 complex can be a planar one, such as $(PR_3)_2M(\eta^2\text{-}CS_2)$ (M = Pd, Pt[35]). In this case the metal has a filled d_{z^2} orbital, and eventually the bonding in the resulting complex 11 could be envisaged in terms of a C–S η^2-bonded linkage supported by a ML_3 fragment.



11

Experimental Section

General Data. All the reactions and manipulations were routinely performed under a nitrogen atmosphere. Literature

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[35] (a) Mason, R.; Rae, A. I. M. *J. Chem. Soc.* **1970**, 1767. (b) Kashiwagi, T.; Yasuoka, N.; Ueki, T.; Kasai, N.; Kakudo, M.; Takahashi, S.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 296.

methods were used for the preparation of (triphos)ClRh(CS$_2$)[5] and (triphos)ClRh(CSe$_2$).[6] THF was purified by distillation over LiAlH$_4$ just before use. All other chemicals and solvents employed were reagent grade and were used without further purification. Hexafluorobut-2-yne was purchased from Strem. The solid complexes were collected on a sintered-glass frit and washed successively with ethanol and petroleum ether before being dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using samples mulled in Nujol between KBr plates. ^{31}P{^{1}H} NMR spectra were taken on a Varian CFT 20 spectrometer. Peak positions are relative to phosphoric acid with downfield values reported as positive. Conductance measurements were made by using a WTW Model LBR/B conductivity bridge in ca. 10^{-3} M nitroethane solutions.

(triphos)ClRhC(CF$_3$)=C(CF$_3$)CSC(CF$_3$)=C(CF$_3$)S (3). Hexafluorobut-2-yne (0.16 g, 1 mmol) was condensed on to a solution of (triphos)ClRh(CS$_2$) (0.42 g, 0.5 mmol) in CH$_2$Cl$_2$ (40 mL) (−196 °C). The reaction mixture was then allowed to warm up to room temperature over 30 min, during this time the color of the solution changed from red-orange to yellow-brown. On addition of ethanol (30 mL) and partial evaporation of the solvent, a crop of yellow crystals separated; yield 90%. Anal. Calcd for C$_{50}$H$_{39}$ClF$_{12}$P$_3$RhS$_2$: C, 51.62; H, 3.37; Rh, 8.84; S, 5.51. Found: C, 51.43; H, 3.38; Rh, 8.73; S, 5.45.

(triphos)ClRhC(CF$_3$)=C(CF$_3$)CSeC(CF$_3$)=C(CF$_3$)Se (4). The procedure described above for compound **3** was successfully employed also for this synthesis; yield 90%. Anal. Calcd for C$_{50}$H$_{39}$ClF$_{12}$P$_3$RhSe$_2$: C, 47.77; H, 3.12; Rh, 8.18; Se, 12.56. Found: C, 47.40; H, 3.08; Rh, 8.05; Se, 12.20.

[(triphos)RhC(CF$_3$)=C(CF$_3$)CSC(CF$_3$)=C(CF$_3$)S]BPh$_4$·CH$_2$Cl$_2$ (5). A mixture of **3** (0.35 g, 0.3 mmol) and TlPF$_6$ (0.11 g, 0.3 mmol) was stirred in acetone (30 mL) for 1 h and then filtered to remove the precipitated TlCl. NaBH$_4$ (0.17 g, 0.5 mmol) and a mixture of butanol and CH$_2$Cl$_2$ (30 mL) were then added to the red filtrate. On slow evaporation of the solvent compound **5** crystallized as red crystals; yield 95%. Anal. Calcd for C$_{75}$H$_{61}$BCl$_2$F$_{12}$P$_3$RhS$_2$: C, 58.82; H, 4.01; Rh, 6.71; S, 4.18. Found: C, 61.20; H, 3.98; Rh, 7.05; S, 4.32.

[(triphos)RhC(CF$_3$)=C(CF$_3$)CSeC(CF$_3$)=C(CF$_3$Se]-BPh$_4$ (6). The preparation of this compound mirrors that of the sulfur analogue; yield 95%. Anal. Calcd for C$_{74}$H$_{59}$BF$_{12}$P$_3$RhSe$_2$: C, 57.68; H, 3.85; Rh, 6.67; Se, 10.24. Found: C, 57.70; H, 3.88; Rh, 6.52; Se, 10.40.

Reaction of 5 or 6 with PPNCl. A solution of **5** or **6** (0.3 mmol) in CH$_2$Cl$_2$ (20 mL) was treated with PPNCl (0.20 g, 0.35 mmol). There was an immediate color change from red to yellow. Addition of ethanol (20 ml) helped the precipitation of yellow crystals of **3** or **4**; yields 98% and 95%, respectively.

X-ray Diffraction Studies. Crystal data for both compounds **3** and **5** are summarized in Table III. A Philips PW 1100 diffractometer with graphite-monochromated radiation was used for experimental work. As a general procedure three standard reflections were collected every 2 h (no appreciable decay of intensities was observed in any case). The data were corrected for Lorentz and polarization effects. Numerical absorption corrections were applied with transmission factors ranging between 0.98–0.77 and 0.96–0.78 for **3** and **5**, respectively. Atomic scattering factors were those tabulated by Cromer and Waber[36] with anomalous dispersion corrections taken from ref 37. The computational work was essentially performed by using the SHELX76 system.[38]

(triphos)ClRhC(CF$_3$)=C(CF$_3$)CSC(CF$_3$)=C(CF$_3$)S (3). A very limited number of reflections with $I > 3\sigma(I)$ (namely, 1334 over a total of 5898 measured reflections) were available for the structure solution and refinement. Initially, a Patterson map and a series of Fourier maps revealed all of the non-hydrogen atoms. The least-squares refinement presented some difficulties on account of the small ratio of reflections to variables (ca. 5). Some constraints were adopted such as rigid-body models (D_{6h}) for all of the phenyl rings and fixed C–C (1.54 Å) within the triphos ligands and the C–CF$_3$ groups of substituted alkynes. Anisotropic thermal parameters were used only for the rhodium atom. Furthermore, the structure is affected by some disorder of the two terminal CF$_3$ groups involving the carbon atoms C(11) and C(12). Alternative orientations with appropriate populations parameters were refined with an evident increase of the number of variables. Altogether, the final structural parameters are affected by high standard deviations. As a final point the possible ambiguity between the space groups $P6_1$ and $P6_5$ was properly checked by comparing at a very late stage of refinement the results of the least-squares method in the two groups. The R factor for $P6_1$ is several units lower than that for $P6_5$. The final difference map was essentially featureless. Final coordinates of all the non-hydrogen atoms are reported in Table IV.

[(triphos)RhC(CF$_3$)=C(CF$_3$)CSC(CF$_3$)=C(CF$_3$)S]BPh$_4$·CH$_2$Cl$_2$ (5). The quality of the data allowed in this case a much better structural refinement. The structure was solved by the Patterson method and Fourier techniques. During the least-squares refinement all the non-hydrogen atoms, with the exception of the phenyl carbon atoms, were allotted anisotropic temperature factors. Also, the phenyl rings were treated as rigid bodies and the hydrogen atoms were introduced at calculated positions. A difference map showed some relatively high peaks which were attributed to two independent dichloromethane solvent molecules. The associated high thermal parameters indicated that the solvent position were probably only partiall occupied. Accordingly the atoms of the two solvent molecules were refined isotropically with occupancy factors 0.5, but no attempt was made to refine those coefficients. The final difference map revealed two peaks, each 0.6 e/Å^3 high, located near the first and sixth phenyl ring of the complex cation. Final coordinates of all non-hydrogen atoms are reported in Table V.

Computational Details. All calculations were of the extended Hückel type[39] using a modified version of the Wolfsberg–Helmholz formula.[40] The parameters for the rhodium atom were the same as in ref 41. Significant geometrical details are given in the text.

Registry No. **1**, 92669-51-7; **2**, 95738-92-4; **3**, 94070-31-2; **4**, 102234-20-8; **5**, 102234-22-0; **6**, 102234-24-2; (CF$_3$)C≡C(CF$_3$), 692-50-2.

Supplementary Material Available: Tables of anisotropic and isotropic temperature factors for **5** and observed and calculated structure factors for **3** and **5** (42 pages). Ordering information is given on any current masthead page.

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(37) *International Tables of Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

(38) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determinations, University of Cambridge, Cambridge, 1976.

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(41) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.