

Rhodium Dithiocarbamate Compounds as Metalloligands: A Controlled Way for the Construction of Binuclear Complexes

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Introduction

Metal dithiocarbamates are the subject of current research activity due to their potential applications and their interesting coordination behavior.¹ There are some examples of dithiocarbamate binuclear compounds, but most complexes are mononuclear in solution, although in some cases crystallize in polymeric forms.² The early preparation of mononuclear rhodium(I and III) dithiocarbamates was reported by Cotton and McCleverty,³ while an interesting example of a binuclear complex is the cation $[\text{Rh}^{\text{III}}_2\{\text{S}_2\text{CN}(\text{Me})_2\}_5]^+$, in which the two rhodium atoms achieve an octahedral environment as a consequence of the additional coordination of two bridging sulfur atoms from two different dithiocarbamate groups (Figure 1A).⁴ Meanwhile, in the related $[\text{Ru}^{\text{III}}_2\{\text{S}_2\text{CN}(\text{Et})_2\}_5]^+$ cation, one of the dithiocarbamate groups acts as an exo-bridging ligand across the Ru–Ru bond (Figure 1B).⁵ Thus, although transition metal complexes containing dithiocarbamate groups as bridging or, most frequently, as chelating ligands are well-known,⁶ the chemical behavior of dithiocarbamate metal complexes as metalloligands remains essentially unexplored. Only very recently, the neutral rhodium and iridium(III) tris(dithiocarbamate) complexes have been described as metalloligands toward the silver cation Ag^+ , forming cationic complexes of the type $[\text{Ag}\{\text{M}(\text{S}_2\text{CNR})_3\}_2]\text{BF}_4$ (M = Rh, Ir).^{1g}

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- (1) (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301. (b) Bond, A. M.; Martin, R. L. *Coord. Chem. Rev.* **1984**, *54*, 23. (c) Heras, J. V.; Pinilla, E.; Ovejero, P. *J. Organomet. Chem.* **1984**, *269*, 277. (d) Cano, M.; Campo, J. A.; Pérez-García, V.; Gutiérrez-Puebla, E. *J. Organomet. Chem.* **1990**, *396*, 49. (e) Bardají, M.; Laguna, A.; Laguna, M.; Merchán, F. *Inorg. Chim. Acta* **1994**, *215*, 215. (f) Price, D. J.; Wali, M. A.; Bruce, D. W. *Polyhedron* **1997**, *16*, 315. (g) Bond, A. M.; Colton, R.; Gatehouse, B. M.; Mah, Y. A. *Inorg. Chim. Acta* **1997**, *260*, 61.
- (2) Bond, A. M.; Colton, R.; Mah, Y. A.; Traeger, J. C. *Inorg. Chem.* **1994**, *33*, 2548 and references therein. Exarchos, G.; Robinson, S. D. *Polyhedron* **1997**, *16*, 1573.
- (3) Cotton, F. A.; McCleverty, J. A. *Inorg. Chem.* **1964**, *3*, 1398.
- (4) Hendrickson, A. R.; Martin, R. L.; Taylor, D. *Aust. J. Chem.* **1976**, *29*, 269.
- (5) Mattson, B. M.; Heiman, J. R.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 564.
- (6) Wilkinson, G.; Guillard, R. D.; McCleverty, J. A., Eds. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, U.K., 1987; Vol. 2, p 585.

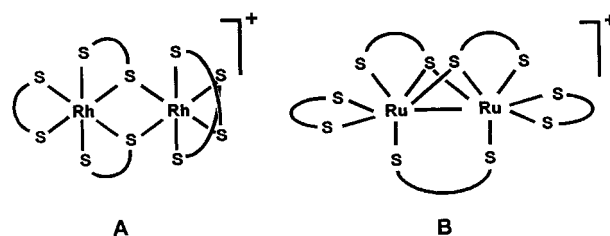


Figure 1. Schematic representations of the different dithiocarbamate coordinations in $[\text{Rh}_2\{\text{S}_2\text{CNMe}_2\}_5]^+$ (A) and $[\text{Ru}_2\{\text{S}_2\text{CNEt}_2\}_5]^+$ (B).

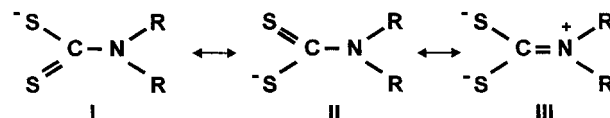


Figure 2. Resonance structures for dithiocarbamate anions.

It is worth keeping in mind that each of the two sulfur atoms of a metal-coordinated chelate dithiocarbamate ligand maintains an additional coordination capability due to the availability of, at least, one pair of potentially bonding electrons. This potentiality has been contemporarily exploited in the coordination chemistry of thiolato and pyridine-2-thiolato complexes allowing the tailored synthesis of homo- and heteronuclear rhodium aggregates.⁷

We report in this paper the synthesis of mononuclear *N*-methyl,*N*-phenyl-dithiocarbamate rhodium complexes and their capacity to act as metalloligands in the controlled construction of binuclear dithiocarbamate-bridged species. The structural parameters of the dithiocarbamate ligand are compared before and after binucleation from the X-ray structures of two complexes.

Results and Discussion

The mononuclear complexes $[\text{Rh}\{\text{S}_2\text{CN}(\text{Me})(\text{Ph})\}(\text{diolfen})]$ (diolfen = 1,5-cyclooctadiene (COD), **1**, and norbornadiene (NBD), **2**) could be easily prepared by reaction of the binuclear rhodium(I) complexes $[\text{Rh}_2(\mu\text{-Cl})_2(\text{diolfen})_2]$ (diolfen = COD, NBD) and $\text{HN}(\text{Et})_3\{\text{S}_2\text{CN}(\text{Me})(\text{Ph})\}$ in a 1:2 molar ratio.

Compounds **1** and **2** have been isolated as yellow or orange microcrystalline solids. The ¹H NMR spectrum of complex **1** shows for the cyclooctadiene ligands four broad signals at δ 4.59 and 4.26 ppm and at δ 2.21 and 1.61 ppm, integrating by 2:2:4:4, respectively. The ¹³C NMR spectrum exhibits two doublets (δ 81.91, 80.60 ppm, J_{RhC} 11 Hz) and two singlets (δ 31.21, 30.02 ppm) corresponding to the olefinic and aliphatic carbon atoms, respectively, of the cyclooctadiene ligand. At δ 212.91 ppm a singlet from the tertiary carbon of the dithiocarbamate ligand also appears. These data indicate that the dithiocarbamate ligand is chelating the rhodium center with a significant contribution of the resonance form III (Figure 2), in such a way that the mononuclear molecule presents inequivalence of the olefinic and also of the aliphatic cyclooctadiene atoms, adopting a C_s symmetry. Additionally, the presence in the IR spectrum of a medium band at 1590 cm^{-1} , corresponding

- (7) Ciriano, M. A.; Pérez-Torrente, J.; Viguri, F.; Lahoz, F. J.; Oro, L. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1493. Ciriano, M. A.; Pérez-Torrente, J.; Oro, L. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1991**, 255. Ciriano, M. A.; Pérez-Torrente, J.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1831.

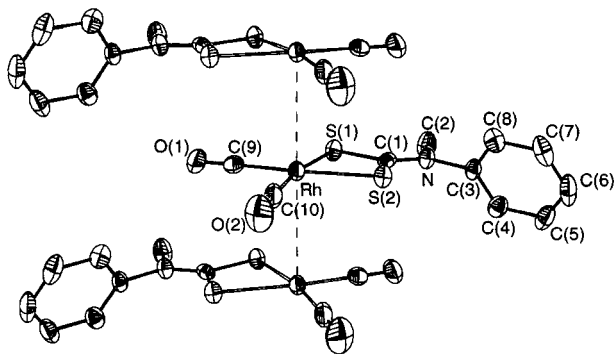


Figure 3. Molecular structure of **3** together with the atomic numbering scheme used. The relative disposition of three contiguous stacked molecules is also shown.

to the $\nu(\text{C}=\text{N})$ stretching frequency, supports the existence of a partially multiple C–N bond.^{3,5,6} The spectroscopic data obtained for compound **2** also suggest a C_s symmetry for this molecule.

Bubbling carbon monoxide through dichloromethane solutions of complexes **1** or **2** leads to the displacement of the coordinated diolefins causing an instantaneous change of color from yellow (**1**) or orange (**2**) to dark yellow, and after addition of diethyl ether, precipitation of dark green microcrystals formulated as $[\text{Rh}\{\text{S}_2\text{CN}(\text{Me})(\text{Ph})\}(\text{CO})_2]$ (**3**) took place.

The spectroscopic data measured for **3** again suggest the coordination of the dithiocarbamate as chelate. The planarity of the dithiocarbamate ligand together with the feeble steric demand of the carbonyl groups and the square-planar coordination of the metal center confer the metal coordination sphere of this molecule a reasonable planarity suitable for the formation of stacked arrangements with potential intermetallic interactions.^{8–11} This proposal is supported by the complex solid-state IR spectrum exhibited by **3** and also by the dark color of the isolated solid.¹²

The formation of a columnar stacking with intermetallic interactions for complex **3** has been definitively determined by an X-ray diffraction study (Figure 3). The molecules are forming almost linear metal chains ($\text{Rh}\cdots\text{Rh}\cdots\text{Rh}$ angle of $179.47(1)^\circ$) with equal $\text{Rh}\cdots\text{Rh}$ distances of $3.2528(7)$ Å (Table 1). This distance is similar to those reported in other stacked rhodium(I) square-planar complexes such as $[\text{Rh}(\text{C}_2\text{O}_4)(\text{CO})_2]^-$, $3.243(1)$ Å,¹⁰ and $[\text{Rh}(\text{acac})(\text{CO})_2]$, 3.253 and 3.271 Å.¹¹ Along the stacking direction each planar molecule is rotated by $131.4(1)^\circ$, in such a way that one carbonyl group is situated bisecting both dithiocarbamate groups of the neighboring molecules. This disposition probably is adopted to minimize the interligand repulsion with respect to an eclipsed disposition as it has been suggested for related d^8 stacked complexes.⁸

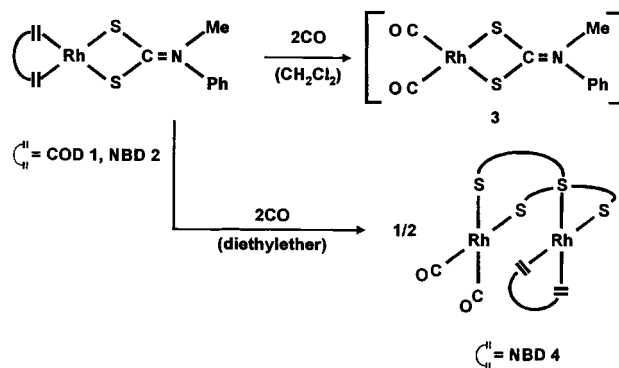
Interestingly, when carbon monoxide is bubbled through a diethyl ether suspension of $[\text{Rh}\{\text{S}_2\text{CN}(\text{Me})(\text{Ph})\}(\text{NBD})]$ (**2**), a dimerization process occurs with formation of the compound formulated as $[\text{Rh}_2\{\mu\text{-S}_2\text{CN}(\text{Me})(\text{Ph})\}_2(\text{CO})_2(\text{NBD})]$ (**4**) (Scheme 1). The expected square-planar coordination for the metal centers in rhodium(I) complexes led us to assume a $\mu\text{-}\eta^1(\text{S}),\eta^1(\text{S}')$ coordination mode^{13–15} for the dithiocarbamate ligands as

Table 1. Selected Bond Distances (Å) and Angles (deg) for **3**^a

Rh···Rh'	3.2528(7)	S(1)–C(1)	1.715(4)
Rh–S(1)	2.3629(14)	S(2)–C(1)	1.718(5)
Rh–S(2)	2.3727(14)	N–C(1)	1.317(6)
Rh–C(9)	1.868(5)	N–C(2)	1.469(6)
Rh–C(10)	1.883(6)	N–C(3)	1.450(5)
S(1)–Rh–S(2)	74.35(4)	S(1)–C(1)–S(2)	113.0(3)
S(1)–Rh–C(9)	96.28(16)	S(1)–C(1)–N	122.6(3)
S(1)–Rh–C(10)	170.47(15)	S(2)–C(1)–N	124.4(3)
S(2)–Rh–C(9)	170.61(16)	C(1)–N–C(2)	122.1(4)
S(2)–Rh–C(10)	97.26(15)	C(1)–N–C(3)	121.5(4)
C(9)–Rh–C(10)	92.0(2)	C(2)–N–C(3)	116.3(4)
Rh–S(1)–C(1)	86.50(17)	Rh–C(9)–O(1)	178.8(4)
Rh–S(2)–C(1)	86.12(15)	Rh–C(10)–O(2)	177.4(5)

^a Primed atoms are related to the unprimed ones by the following symmetry transformation: $1/2 + x, 1/2 - y, z$.

Scheme 1



the most probable for this compound although other molecular arrangements could not be excluded.

Preparation of Binuclear Species. An effective synthetic way to prepare species of higher nuclearity consists of the incorporation of metal fragments into metalloligands.^{7,16} In this context we have explored the ability of the previously described mononuclear rhodium(I) dithiocarbamate complexes to coordinate an additional metal fragment giving rise to binuclear species. These mononuclear complexes are expected to behave as metalloligands due to the potentiality of the sulfur atoms of the dithiocarbamate group to act as η^2 -bridging centers.

With this idea in mind, we have studied the reactivity of the mononuclear compounds $[\text{Rh}\{\text{S}_2\text{CN}(\text{Me})(\text{Ph})\}\text{L}_2]$ ($\text{L}_2 = \text{COD}$ (**1**), $(\text{CO})_2$ (**3**)) toward the cationic solvate rhodium(I) species $[\text{Rh}(\text{COD})(\text{acetone})_n]^+$. These reactions give rise to binuclear complexes of formula $[\text{Rh}_2\{\mu\text{-S}_2\text{CN}(\text{Me})(\text{Ph})\}(\text{COD})\text{L}_2]\text{BF}_4$ ($\text{L}_2 = \text{COD}$ (**5**), $(\text{CO})_2$ (**6**)) (Scheme 2). Their formulation as binuclear complexes is consistent with their mass spectrometry measurements and has been definitively confirmed for compound **5** by X-ray diffraction.

The cationic complex in **5** is formed by two “Rh(COD)” fragments linked through the dithiocarbamate anion acting as a bridging $\eta^2,\eta^2(\text{S},\text{S}')$ ligand. Each metal is in a square-planar

- (8) Alvarez, S.; Aullón, G. *Chem. Eur. J.* **1997**, *3*, 655.
 (9) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1.
 (10) Real, J.; Bayón, J. C.; Lahoz, F. J.; López, J. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1889.
 (11) Bailey, N. A.; Coates, E.; Robertson, G. B.; Bonati, F.; Ugo, R. *J. Chem. Soc., Chem. Commun.* **1967**, 1041. Huq, S.; Skapski, A. C. *Cryst. Mol. Struct.* **1974**, *4*, 411.

- (12) Bonati, F.; Oro, L. A.; Pinillos, M. T.; Aprea, M. C.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1989**, *369*, 253.
 (13) Bardají, M.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M. *Organometallics* **1994**, *13*, 3415.
 (14) Lei, X.; Huang, Z.; Liu, Q.; Hong, M.; Liu, H. *Inorg. Chem.* **1989**, *28*, 4302.
 (15) Heinrich, D. D.; Wang, J.; Fackler, J. P. *Acta Crystallogr., C* **1990**, *46*, 1444.
 (16) Elduque, A.; Navarro, N.; Oro, L. A.; Pinillos, M. T. *Anal. Quím. Int. Ed.* **1996**, *92*, 349. Tejel, C.; Villarroya, B. E.; Ciriano, M. A.; Oro, L. A.; Lanfranchi, M.; Tiripicchio A.; Tiripicchio-Camellini, M. *Inorg. Chem.* **1996**, *35*, 1782.

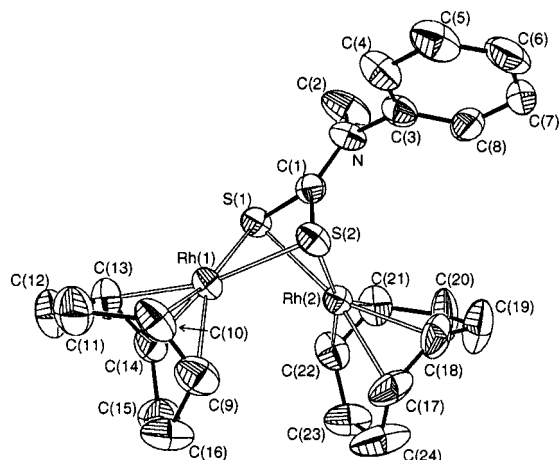
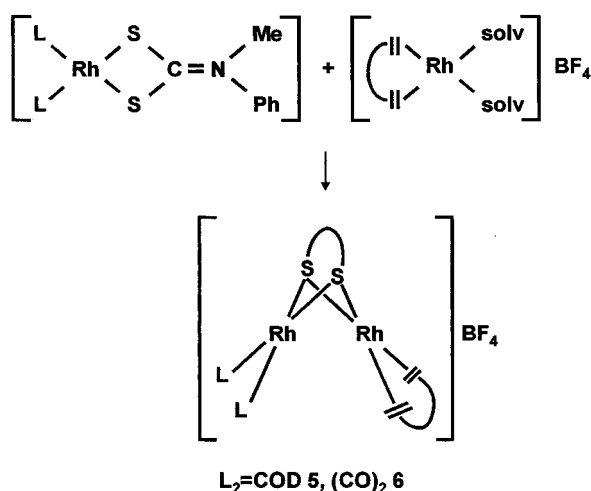


Figure 4. Molecular drawing of the binuclear cationic complex of **5** showing the labeling scheme.

Scheme 2



environment, coordinated to a cyclooctadiene ligand and to both sulfur atoms of the dithiocarbamate bridging group (Figure 4). Although examples of an $\eta^1(S), \eta^1(S')$ ^{13,14,17} and also of an $\eta^1(S), \eta^2(S, S')$ ^{13,18} coordination modes of the dithiocarbamate groups in transition metal complexes have been described, complex **5** is the first dithiocarbamate compound crystallographically characterized exhibiting a $\mu\text{-}\eta^2, \eta^2(S, S')$ coordination. In this complex both sulfur atoms are bonded to both metal centers furnishing formally eight electrons to the binuclear entity.

The most intriguing feature of this molecular structure is the asymmetrical coordination of the bridging ligand, showing the C(sp²) plane of the dithiocarbamate ligand nearly coplanar with the coordination plane of Rh(1) (dihedral angle 160.4(3)°) but almost perpendicular to that of the second rhodium atom (101.2(3)°). This structural disposition brings about the intermetallic distance to be very short (2.8948(10) Å; see Table 2), in the range described for short intermetallic bonding interactions that, in some cases, have been confirmed by theoretical calculations.¹⁹

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **5**

Rh(1)···Rh(2)	2.8948(10)		
Rh(1)–S(1)	2.3679(18)	Rh(2)–S(1)	2.387(2)
Rh(1)–S(2)	2.3686(18)	Rh(2)–S(2)	2.4050(19)
Rh(1)–C(9)	2.158(8)	Rh(2)–C(17)	2.135(7)
Rh(1)–C(10)	2.150(7)	Rh(2)–C(18)	2.141(8)
Rh(1)–C(13)	2.171(7)	Rh(2)–C(21)	2.144(7)
Rh(1)–C(14)	2.145(7)	Rh(2)–C(22)	2.146(7)
S(1)–C(1)	1.741(7)	S(2)–C(1)	1.756(7)
C(9)–C(10)	1.397(13)	C(17)–C(18)	1.382(12)
C(13)–C(14)	1.381(11)	C(21)–C(22)	1.367(10)
N–C(1)	1.314(8)	N–C(2)	1.478(9)
N–C(3)	1.452(9)		
S(1)–Rh(1)–S(2)	73.93(6)	S(1)–Rh(2)–S(2)	72.92(6)
S(1)–Rh(1)–M(1) ^a	170.9(3)	S(1)–Rh(2)–M(3) ^a	173.3(3)
S(1)–Rh(1)–M(2) ^a	99.4(3)	S(1)–Rh(2)–M(4) ^a	98.3(3)
S(2)–Rh(1)–M(1) ^a	98.8(3)	S(2)–Rh(2)–M(3) ^a	100.9(3)
S(2)–Rh(1)–M(2) ^a	171.3(3)	S(2)–Rh(2)–M(4) ^a	168.7(3)
M(1)–Rh(1)–M(2) ^a	87.3(4)	M(3)–Rh(2)–M(4) ^a	87.5(4)
Rh(1)–S(1)–C(1)	75.00(6)	Rh(2)–S(2)–Rh(1)	74.66(5)
Rh(1)–S(1)–C(10)	86.6(2)	Rh(1)–S(2)–C(1)	86.2(2)
Rh(2)–S(1)–C(1)	68.8(2)	Rh(2)–S(2)–C(1)	68.1(2)
S(1)–C(1)–S(2)	109.1(4)	C(1)–N–C(2)	119.8(6)
S(1)–C(1)–N	125.8(5)	C(1)–N–C(3)	120.9(6)
S(2)–C(1)–N	125.1(5)	C(2)–N–C(3)	118.6(6)

^a M(1), M(2), M(3), and M(4) represent the midpoints of the olefinic bonds C(9)–C(10), C(13)–C(14), C(17)–C(18), and C(21)–C(22), respectively.

This conformation also causes a relatively short Rh(2)–C(1) distance (2.389(7) Å) which led us to think about the possibility of a $\mu\text{-}\eta^3(S, C, S')$ coordination mode of the dithiocarbamate ligand, similar to that previously observed for the related S₂CPR₃ ligands.²⁰

The distances Rh(1)–S (2.3679 and 2.3686(18) Å) are equal to those observed for compound **3** (2.3629 and 2.3727(14) Å) and are very similar to those previously described for the binuclear rhodium(III) complex [Rh₂($\mu\text{-dppe}$)(S₂CNEt₂)₂(C₅-Me₅)₂]²⁺, 2.3493 and 2.3638(18) Å, where the dithiocarbamate anions are coordinated as chelates.²¹ However, the Rh(2)–S distances are slightly longer (2.387(2) and 2.4050(19) Å), probably originated by the perpendicular coordination of the dithiocarbamate ligand.

The S–C bond lengths are also correlated with the coordination mode of the sulfur atoms. Thus, the distances presented by the mononuclear compound **3** are slightly shorter (1.715(4) and 1.718(5) Å) than those observed in the binuclear complex **5** (1.741(7) and 1.756(7) Å). Probably, the multiple S–C bond contribution present in the mononuclear compound **3** (Figure 2, forms I and II) has to decrease, or even disappear, in the binuclear compound **5**, due to the coordination of the S atoms to the second metal center through the same p-orbitals previously involved in **3** in the dithiocarbamate S–C(N)–S π -bonding system.

Expecting that some insight about the possible interaction between the tertiary carbon of the dithiocarbamate ligand and one rhodium center could be obtained, we performed ¹H and ¹³C{¹H} NMR spectra measurements of complex **5**, decreasing the temperature to –60 °C. No changes in the spectra were observed from room temperature to –60 °C. All the ¹³C{¹H} NMR spectra of complex **5** show the signal of the central carbon

- (17) Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946. Iwasaki, H. *Acta Crystallogr.* **1973**, *B29*, 2115.
 (18) Goel, A. B.; Goel, S.; VanDerveer, D.; Brinkley, C. G. *Inorg. Chim. Acta* **1982**, *64*, L173. Pignolet, L. H.; Wheeler, S. H. *Inorg. Chem.* **1980**, *19*, 935. Ieperuma, O. A.; Felthour, R. D. *Inorg. Chem.* **1975**, *14*, 3042. Landgrafe, C.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1994**, 1885.
 (19) Masdeu, A. M.; Ruiz, A.; Castellón, S.; Claver, C.; Hitchcock, P. B.; Chaloner, P. A.; Bó, C.; Poblet, J. P.; Sarasa, P. *J. Chem. Soc., Dalton Trans* **1993**, 2689.

- (20) Galindo, A.; Gutierrez-Puebla, E.; Monge, A.; Pastor, A.; Pizzano, A.; Ruiz, C.; Sánchez, L.; Carmona, E. *Inorg. Chem.* **1993**, *32*, 5569. Miguel, D.; Pérez-Martínez, J. A.; Riera, V. *Organometallics* **1993**, *12*, 1394. López, E. M.; Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *J. Organomet. Chem.* **1995**, *492*, 23.
 (21) Blake, A. J.; Fotheringham, J. D.; Stephenson, T. A.; Hambling, S. G.; Sawyer, L. *Acta Crystallogr.* **1991**, *C47*, 648.

of the S_2CNR_2 ligand as a singlet at 178.89 ppm excluding any rhodium–carbon bonding interaction. This signal appears at a δ value similar to that of compound **1** which exhibits a chelating S,S' coordination mode for the dithiocarbamate ligand, and it is far from the higher field resonance detected in related complexes showing an $\eta^3(S,C,S')$ coordination.²⁰ The cyclooctadiene carbon resonances appear as four doublets (J_{RhC} 11 Hz) for the olefinic carbon atoms and as four singlets for the aliphatic carbon atoms, according with a C_s symmetry for compound **5**. In addition, the 1H NMR spectrum of **5**, and those obtained for **6** (1H and ^{13}C), also agree with this proposal.

In consequence, it seems reasonable to propose that in solution, in the NMR time scale, the dithiocarbamate ligand in **5** and **6** is symmetrically bonding to the two metal centers. This can be due to a rapid oscillation, even at -60 °C, of the dithiocarbamate CNR_2 moiety at both sides of the ideal plane defined by the two S atoms and the middle point of the Rh–Rh vector, as it has been observed in binuclear alkynyl complexes.²² Another possibility to explain this behavior could consider a static symmetrical bridging coordination as the most stable situation for this type of bonding mode, despite the observed asymmetric solid-state structure.

Taking into account the above results, it seems that the Rh(2)–C(1) distance obtained in the solid state, although relatively short, is not representative of an $\eta^3(S,C,S')$ coordination mode. At this point, two interrelated questions arise: If there is not interaction between the central carbon and the rhodium atom Rh(2), why is the solid-state structure asymmetrical, and what type of movement—if existent—is responsible for the C_s symmetry observed in solution?

We have performed some theoretical calculations with a simplified model $[Rh_2\{\mu-S_2CN(Me)_2\}(CO)_4]^+$, built up with the bond lengths and angles deduced from both X-ray determinations. Using the extended Hückel approach,²³ the Walsh diagram for the oscillation movement of the dithiocarbamate ligand around the S–S axis has been evaluated, and we have found the symmetrical bridging situation to be the most stable. Without modifying the bridging ligand geometry or that of both “Rh(CO)₂” units, we have calculated the energy of the different conformations obtained by rotating any of the three fragments around the S–S axis and, in consequence, varying the dihedral angles between the dithiocarbamate ligand and each Rh(CO)₂ groups (α and β) (Figure 5). The calculation performed evidences a particular flat potential energy well indicating a relative conformational freedom for the hypothetical movement analyzed. The shape of this potential energy well (Figure 5) shows any conformational motion of L (CNMePh) varying α , and consequently β , along the line *a* ($\alpha + \beta = 250^\circ$, $105 \leq \alpha$, $\beta \leq 145^\circ$) to be nearly isoenergetical; however any conformational change perpendicular to line *a* (that is, implying a modification of the dihedral angle between the two metal coordination planes and consequently the intermetallic separation) results energetically unfavorable. If the oscillation of L around the S–S axis is not energetically demanding under the limits described above, this movement should be taking place in solution even at low temperature and would confer the molecule an apparently static C_s symmetry. In the solid state the packing forces could presumably bring the conformation of the molecule slightly out of the potential energy well to the

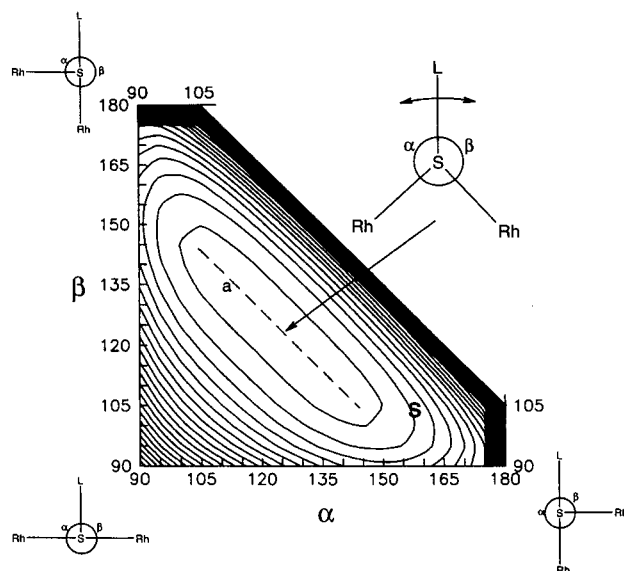


Figure 5. Potential energy map calculated from the model $[Rh_2\{\mu-S_2CN(Me)_2\}(CO)_4]^+$ for conformers differing in the relative dihedral angles (α and β) between the dithiocarbamate $CNMe_2$ moiety and the two metal coordination planes. S represents the position of the solid-state structure. Isoenergetic contours are drawn at 0.1 eV intervals.

asymmetric disposition determined. In fact, the conformation found in the solid state ($\alpha = 160.4(3)$, $\beta = 101.2(3)^\circ$) is only ca. 8 kJ mol⁻¹ higher in energy than the minimum calculated $\alpha = \beta \approx 125^\circ$.

Another dynamical alternative to generate the solution C_s symmetry observed for **5** and **6** could imply the rotation of the phenyl and methyl groups around the CN bond of the dithiocarbamate ligand. We have also evaluated the Walsh diagrams for this rotation using the same model and approach and starting from both conformations: the symmetrical (proposed to exist in solution) and the asymmetrical (found in the solid state). The energy activation barrier calculated for this rotation is in both cases approximately 42–63 kJ mol⁻¹; most probably, this barrier is high enough to avoid the movement to take place at room temperature and, consequently, to be observed in the NMR experiments.

In conclusion, the present paper has shown the ability of mononuclear rhodium dithiocarbamate compounds to act as metalloligands, allowing the construction of binuclear complexes in a controlled way. In addition, the X-ray studies have revealed a novel bridging $\eta^2, \eta^2(S,S')$ coordination mode for the dithiocarbamate ligand and a columnar stacking of the mononuclear complex $[Rh\{S_2CN(Me)(Ph)\}(CO)_2]$ assembled with clear $Rh \cdots Rh$ intermolecular interactions.

Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). $[Rh_2(\mu-Cl)_2(COD)_2]$ ²⁴ and $[Rh_2(\mu-Cl)_2(NBD)_2]$ ²⁵ were prepared according to literature methods. Solvents were purified according to standard procedures and distilled under nitrogen prior to use. All other reagents were purchased and used without further purification. Solution and Nujol mull infrared spectra were recorded on a Nicolet Magna 550 spectrometer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000, or a Bruker ARX 300 MHz spectrometer. 1H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative

(22) Esteruelas, M. A.; Lahuerta, O.; Modrego, J.; Nurnberg, O.; Oro, L. A.; Rodríguez, L.; Sola, E.; Werner, H. *Organometallics* **1993**, *12*, 266 and references therein.

(23) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179; **1962**, *37*, 2872.

(24) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(25) Abel, E. W.; Bernetti, M. A.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3178.

to Me₄Si. ³¹P{¹H} NMR spectra were measured relative to H₃PO₄ (85%). Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. Fast atom bombardment (FAB) mass spectra were recorded on a AUTOSPEC V6 spectrometer.

Preparation of HNEt₃{S₂CN(Me)(Ph)}. A mixture of NEt₃ (10 g, 0.130 mmol) and HNMePh (10 g, 0.093 mmol) in diethyl ether (15 mL) was added dropwise into a CS₂ (30 g) solution leading to the formation of a yellow precipitate. The solid was isolated by filtration, washed with cold diethyl ether, and vacuum-dried (12 g, 34%). Anal. Calcd for C₁₄H₂₄N₂S₂: C, 59.31; H, 8.17; N, 9.88; S, 22.61. Found: C, 59.33; H, 8.55; N, 9.86; S, 21.62. IR (cm⁻¹, Nujol mulls): 1590 [ν(CN)]. ¹H NMR (CDCl₃): δ 7.26 (m, 5H, Ph), 3.79 (s, 3H, Me), 3.19 (q, 6H, N(CH₂CH₃)₃, J_{HH} 7.4), 1.32 (t, 9H, N(CH₂CH₃)₃, J_{HH} 7.4).

Preparation of [Rh{S₂CN(Me)(Ph)}(COD)] (1). A solution of HNEt₃{S₂CN(Me)(Ph)} (460 mg, 1.62 mmol) in dichloromethane (10 mL) was added to a solution of [Rh₂(μ-Cl)₂(COD)₂] (400 mg, 0.81 mmol) in acetone (15 mL). The initial orange solution transformed immediately to a yellow suspension which was stirred for 30 min. Evaporation of the solvents to dryness and addition of methanol (15 mL) allowed the complete precipitation of a yellow solid which was filtered out, washed with cold methanol, and vacuum-dried (575 mg, 90%). Anal. Calcd for C₁₆H₂₀NRhS₂: C, 48.85; H, 5.12; N, 3.56; S, 16.30. Found: C, 48.86; H, 5.19; N, 3.65; S, 16.16. FAB (*m/z*): 393 (calcd for C₁₆H₂₀NRhS₂: 393.367). IR (cm⁻¹, Nujol mulls): 1590 [ν(CN)]. ¹H NMR (CDCl₃): δ 6.95 (m, 5H, Ph), 4.59 (s, 2H, CH=, COD), 4.26 (s, 2H, CH=, COD), 3.08 (s, 3H, Me), 2.21 (s, 4H, CH₂, COD), 1.61 (s, 4H, CH₂, COD). ¹³C NMR (CDCl₃): δ 212.91 (s, NCS₂), 142.21 (s, Ph), 129.45 (s, Ph), 128.60 (s, Ph), 126.32 (s, Ph), 81.91 (d, CH=, COD, J_{RhC} 11), 80.60 (d, CH=, COD, J_{RhC} 11), 40.70 (s, Me), 31.21 (s, CH₂, COD), 30.02 (s, CH₂, COD).

Preparation of [Rh{S₂CN(Me)(Ph)}(NBD)] (2). Complex **2** was prepared by the same method described for complex **1** starting from HNEt₃{S₂CN(Me)(Ph)} (370 mg, 1.30 mmol) and [Rh₂(μ-Cl)₂(NBD)₂] (300 mg, 0.65 mmol). The complex was isolated as an orange solid (382 mg, 78%). Anal. Calcd for C₁₅H₁₆NRhS₂: C, 47.74; H, 4.27; N, 3.71; S, 16.99. Found: C, 47.57; H, 3.94; N, 4.21; S, 16.40. FAB (*m/z*): 377 (calcd for C₁₅H₁₆NRhS₂: 377.325). IR (cm⁻¹, Nujol mulls): 1590 [ν(CN)]. ¹H NMR (CDCl₃): δ 7.00 (m, 5H, Ph), 3.88 (m, 4H, CH=, NBD), 3.40 (b, 2H, CH, NBD), 3.13 (s, 3H, Me), 1.68 (m, 2H, CH₂, NBD).

Preparation of [Rh{S₂CN(Me)(Ph)}(CO)₂] (3). Method 1. Carbon monoxide was bubbled through a solution of [Rh{S₂CN(Me)(Ph)}(COD)] (500 mg, 1.46 mmol) in dichloromethane (20 mL), during 30 min, to give first a dark yellow solution and finally a dark green suspension. Concentration of the solvent to ca. 1 mL and addition of diethyl ether (4 mL) allowed the complete precipitation of a dark green solid, which was separated by filtration, washed with cold diethyl ether, and vacuum-dried (310 mg, 71%). Anal. Calcd for C₁₀H₈NO₂RhS₂: C, 35.20; H, 2.36; N, 4.10; S, 18.79. Found: C, 35.90; H, 2.82; N, 3.94; S, 18.67. FAB (*m/z*): 341 (calcd for C₁₀H₈NO₂RhS₂: 341.204). IR (cm⁻¹, Nujol mulls): 1989, 1995, 2043 and 2054 [ν(CO)]. IR (cm⁻¹, CH₂Cl₂): 1990 and 2050 [ν(CO)]. ¹H NMR (CDCl₃): δ 7.37 (m, 5H, Ph), 3.66 (s, 3H, Me).

Method 2. Through a solution of [Rh{S₂CN(Me)(Ph)}(NBD)] (300 mg, 0.79 mmol) in dichloromethane (20 mL), carbon monoxide was bubbled during 45 min. The initial yellow solution transformed to a dark yellow solution and finally to a green suspension. Evaporation of the solvent and addition of diethyl ether (5 mL) gave a dark green solid, which was filtered and vacuum-dried (151 mg, 56%).

[Rh₂{μ-S₂CN(Me)(Ph)}₂(CO)₂(NBD)] (4). Carbon monoxide was bubbled through a suspension of [Rh{S₂CN(Me)(Ph)}(NBD)] (300 mg, 0.79 mmol) in diethyl ether (20 mL) during 20 min. Hexane (20 mL) was added to the resulting dark suspension which was kept in CO atmosphere for 2 days at 5 °C. The resulting orange-brown solid was separated by filtration, washed with hexane, and vacuum-dried (233 mg, 44%). Anal. Calcd for C₂₅H₂₄N₂O₂Rh₂S₄: C, 41.79; H, 3.36; N, 3.89; S, 17.85. Found: C, 42.26; H, 2.90; N, 3.23; S, 17.70. FAB (*m/z*): 718 (calcd for C₂₅H₂₄N₂O₂Rh₂S₄: 718.529). IR (cm⁻¹, CH₂-Cl₂): 2060 and 1995 [ν(CO)], 1590 [ν(CN)]. ¹H NMR (C₆D₆): δ 7.30 (m, 10H, Ph), 6.05 (m, 4H, CH=, NBD), 4.23 (b, 2H, CH, NBD), 3.41 (b, 6H, Me), 1.49 (b, 2H, CH₂, NBD).

Table 3. Crystallographic Data for [Rh{S₂CN(Me)(Ph)}(CO)₂] (**3**) and [Rh₂{μ-S₂CN(Me)(Ph)}(COD)₂]BF₄ (**5**)

	3	5
chem formula	C ₁₀ H ₈ NO ₂ RhS ₂	C ₂₄ H ₃₂ BF ₄ NRh ₂ S ₂
fw	341.20	691.26
temp, K	233.0(2)	283.0(2)
space group	<i>Pna</i> 2 ₁ (No. 33)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	6.5055(12)	13.086(2)
<i>b</i> , Å	17.153(4)	14.048(3)
<i>c</i> , Å	10.8222(13)	14.533(4)
β, deg	90	105.933(18)
<i>V</i> , Å ³	1207.7(4)	2569.0(10)
<i>Z</i>	4	4
ρ _{calcd} , g cm ⁻³	1.877	1.787
μ(Mo Kα), mm ⁻¹	1.742	1.490
<i>R</i> (<i>F</i>) [<i>F</i> ² > 2σ(<i>F</i> ²)] ^a	0.0241	0.0462
w <i>R</i> (<i>F</i> ²) (all data) ^b	0.0532	0.1227
<i>S</i> (all data) ^c	1.035	0.996

^a *R*(*F*) = Σ(|*F*_o| - |*F*_c|)/Σ|*F*_o|, for 1733 and 3205 observed reflections. ^b w*R*(*F*²) = (Σ[w(*F*_o² - *F*_c²)]/Σ[w(*F*_o²)])^{1/2}. ^c *S* = [Σ[w(*F*_o² - *F*_c²)]/(*n* - *p*)]^{1/2}; *n* = number of reflections, *p* = number of parameters.

[Rh₂{μ-S₂CN(Me)(Ph)}(COD)₂]BF₄ (5). Addition of a solution of [Rh(COD)(acetone)_n]⁺ (0.40 mmol) (prepared by reaction of AgBF₄ (77.87 mg, 0.4 mmol) and [Rh₂(μ-Cl)₂(COD)₂] (98.61 mg, 0.20 mmol) in acetone (10 mL)) to a solution of [Rh{S₂CN(Me)(Ph)}(COD)] (157 mg, 0.40 mmol) also in acetone (10 mL) caused immediately the formation of an orange solution which was stirred for 15 min. Evaporation of the solvent to ca. 1 mL and addition of diethyl ether (5 mL) allowed the precipitation of a red-orange solid, which was filtered out, washed with diethyl ether, and vacuum-dried (202 mg, 73%). Anal. Calcd for C₂₄H₃₂NBF₄Rh₂S₂: C, 41.70; H, 4.66; N, 2.02; S, 9.27. Found: C, 41.60; H, 4.71; N, 1.89; S, 9.20. FAB (*m/z*): 604 (calcd for C₂₄H₃₂NRh₂S₂⁺: 604.456). ¹H NMR (CDCl₃): δ 6.83 (m, 5H, Ph), 4.97 (s, 2H, CH=, COD), 4.84 (s, 2H, CH=, COD), 4.73 (s, 2H, CH=, COD), 4.69 (s, 2H, CH=, COD), 3.71 (s, 3H, Me), 2.46 (m, 8H, CH₂, COD), 2.10 (m, 8H, CH₂, COD). ¹³C NMR (CDCl₃): δ 178.89 (s, NCS₂), 141.61 (s, Ph), 130.82 (s, Ph), 130.35 (s, Ph), 124.42 (s, Ph), 85.47 (d, CH=, COD, J_{RhC} 11), 84.90 (d, CH=, COD, J_{RhC} 11), 84.62 (d, CH=, COD, J_{RhC} 11), 83.98 (d, CH=, COD, J_{RhC} 11), 45.75 (s, Me), 31.59 (s, CH₂, COD), 31.39 (s, CH₂, COD), 30.76 (s, CH₂, COD), 29.18 (s, CH₂, COD).

[Rh₂{μ-S₂CN(Me)(Ph)}(COD)(CO)₂]BF₄ (6). A solution of [Rh(COD)(acetone)_n]⁺ (0.44 mmol) (prepared by reaction of AgBF₄ (85.65 mg, 0.44 mmol) and [Rh₂(μ-Cl)₂(COD)₂] (108.47 mg, 0.22 mmol) in acetone (10 mL)) was added dropwise to a solution of [Rh{S₂CN(Me)(Ph)}(CO)₂] (150.13 mg, 0.44 mmol) also in acetone (10 mL). After 10 min of stirring the solution became darker. Evaporation of the solvent and addition of diethyl ether led a dark blue solid, which was filtered out, washed with diethyl ether, and vacuum-dried (104 mg, 75%). Anal. Calcd for C₁₈H₂₀NBF₄O₂Rh₂S₂: C, 33.82; H, 3.15; N, 2.19; S, 10.03. Found: C, 34.00; H, 2.69; N, 2.23; S, 9.77. FAB (*m/z*): 552 (calcd for C₁₈H₂₀NO₂Rh₂S₂⁺: 552.294). IR (cm⁻¹, CH₂-Cl₂): 2004 and 2068 [ν(CO)]. ¹H NMR (CDCl₃): δ 7.39 (m, 5H, Ph), 4.99 (s, 1H, CH=, COD), 4.84 (s, 1H, CH=, COD), 4.74 (s, 1H, CH=, COD), 4.63 (s, 1H, CH=, COD), 3.72 (s, 3H, Me), 2.57 (m, 4H, CH₂, COD), 2.13 (m, 4H, CH₂, COD).

X-ray Structural Analyses of Complexes [Rh{S₂CN(Me)(Ph)}(CO)₂] (3) and [Rh₂{μ-S₂CN(Me)(Ph)}(COD)₂]BF₄ (5). A summary of crystal data and refinement parameters is reported in Table 3. Data were collected on a Siemens-Stoe AED-2 four circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), using in both cases the ω/2θ scan method. A set of three standard reflections were monitored every 60 min of measured time throughout data collection; no important variations were observed. All data were corrected for Lorentz and polarization effects and for absorption using a semiempirical method (minimum and maximum transmission factors 0.599 and 0.647 for **3**; 0.576 and 0.666 for **5**).²⁶ Both structures were solved by direct methods²⁷ and Fourier techniques and refined by full-matrix least squares on *F*² (SHELXL-97).²⁸ Atomic scattering factors,

corrected for anomalous dispersion, were used as implemented in the refinement program.

Data for 3. A dark green prismatic block ($0.22 \times 0.14 \times 0.10$ mm) was indexed to orthorhombic symmetry. Data were collected in the range $4 \leq 2\theta \leq 50^\circ$ ($0 \leq h \leq 7$, $0 \leq k \leq 20$, $0 \leq l \leq 12 + \text{Friedel}$); 2793 measured reflections, 2137 unique ($R_{\text{int}} = 0.0185$). Anisotropic displacement parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were introduced in calculated positions ($\text{C-H} = 0.94$ and 0.97 \AA) and refined riding on the corresponding carbon atoms. Those of the methyl group were clearly observed disordered in two groups with identical occupancy. Weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ ($P = (F_o^2 + 2F_c^2)/3$) with $x = 0.0231$ and $y = 0.1942$. Final agreement factors were $R(F) = 0.0241$ (1733 observed reflections, $F_o^2 < 2\sigma(F_o^2)$) and $wR = 0.0532$ (all data) for 148 parameters. The largest peak in the final difference map is 0.25 e \AA^{-3} .

Data for 5. An orange long needle ($1.50 \times 0.11 \times 0.07$ mm) was mounted on the top of a fiber glass, and a set of randomly searched reflections were indexed to monoclinic symmetry. Data were collected in the range $3 \leq 2\theta \leq 50^\circ$ ($-15 \leq h \leq 14$, $0 \leq k \leq 16$, $0 \leq l \leq 17$); 5016 measured reflections, 4527 unique ($R_{\text{int}} = 0.0536$). After refinement of all non-hydrogen atoms with anisotropic displacement parameters (excepting those of the disordered BF_4 anion), the hydrogen atoms were positioned in calculated positions. As exceptions, the hydrogens of the olefinic carbons bonded to the metals were included

from observed positions. All hydrogens were treated in the refinement riding on the corresponding carbon atoms. The BF_4 anion was found to be disordered and was modeled on the base of three isotropic BF_4 groups with complementary occupancy factors and internal distances restricted to tetrahedral geometry. The weighting scheme used was analogous to that of **3** ($x = 0.055$ and $y = 10.9881$). Final agreement factors were $R(F) = 0.0462$ (3205 observed reflections, $F_o^2 < 2\sigma(F_o^2)$) and $wR = 0.1227$ (all data) for 317 parameters. Maximum and minimum residual peaks in the final difference map were 0.70 and -0.88 e \AA^{-3} .

Molecular Orbital Calculations. Calculations of the extended Hückel type²³ were carried out using a modified version of the Wolfsberg–Helmholz formula.²⁹ The following bond distances (\AA) were used in the model: $\text{Rh-S} = 2.368$, $\text{Rh-C} = 1.874$, $\text{S-C} = 1.710$, $\text{C=N} = 1.317$, $\text{N-C} = 1.470$, $\text{C=O} = 1.126$, and $\text{C-H} = 1.08$. The calculations were made with the CACAO program,³⁰ and the atomic parameters used were those implemented in this program.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **3** and **5** are available on the Internet only. Access information is given on any current masthead page.

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(26) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

(27) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(28) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(29) Ammeter, J. H.; Bürgi, H. B.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(30) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.