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Crystal and Molecular Structure of Dichlorobis(nitrosobenzene)palladium(II), a Nitrogen-Bonded Arylnitrosometal Complex

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The structure of dichlorobis(nitrosobenzene)palladium(II) has been established by a three-dimensional single-crystal X-ray study. Crystals of $(C_6H_5NO)_2PdCl_2$ are monoclinic with $a = 5.782$ (4), $b = 14.657$ (9), $c = 8.118$ (5) Å, and $\beta = 138.84$ (3)°. The space group is $P2_1/c$; observed and calculated ($Z = 2$) densities are 1.84 (2) and 1.90 g/cm^3. The structural analysis was based upon 1601 independent nonzero intensity data collected by counter methods. Full-matrix anisotropic least-squares refinement converged to a final conventional R factor of 0.024. The crystal structure is made up of centrosymmetric monomers, with square-planar coordination about the palladium atom. The monomeric nitrosobenzene ligand is coordinated solely through its nitrogen atom. Principal bond distances include Pd–Cl = 2.295 (1) Å, Pd–N = 1.994 (2) Å, and N–O = 1.209 (3) Å. The phenyl ring is twisted by 11.8° from the C(phenyl)–N–O plane.

Introduction

The reaction of nitrosobenzene with *trans*-$(C_6H_5CN)_2 \cdot PdCl_2$ or with $PdCl_4^{2-}$ has been shown to yield a complex formulated as $(C_6H_5NO)_2PdCl_2$.[1] Spectroscopic data were insufficient to distinguish among the various alternative structural possibilities for this compound. These alternatives include cis or trans stereochemistry, binding of the ligand *via* N or O or through both atoms, and coordination of the nitrosobenzene in its monomeric or dimeric form.

Previous examples of transition metal complexes of nitrosobenzene or substituted nitrosobenzenes are relatively few, even though the $C_6H_5NOFe(CN)_5{}^{3-}$ anion has long been known.[2] A series of substituted nitrosobenzene–iron carbonyl complexes of stoichiometry $LFe(CO)_3$ have been obtained by irradiation of iron pentacarbonyl in the presence of substituted nitrobenzenes.[3,4] One of these complexes has been shown by a crystal structure analysis to have a dimeric structure with bridging nitrosobenzene ligands.[5] Both the nitrogen and oxygen atoms of the nitroso group were shown to be metal coordinated. Mossbauer effect studies have been interpreted as implying similar structures for all of the other substituted nitrosobenzene–iron carbonyl complexes.[6] A number of metal complexes of *p*-nitroso-*N*,*N*-dimethylaniline have also been reported;[7-11] in all of these compounds the NO group is believed to be involved in metal coordination, though the distinction between N and O bonding is not always clear.

Our investigation of the crystal structure of dichlorobis(nitrosobenzene)palladium(II) was motivated by the uncertainty as to the nature of this particular molecular structure, by the lack of structural data on metal-RNO complexes, and by the possible pertinence of the structures of such complexes to studies of the reactions of coordinated nitrosyl groups.[12-16]

Experimental Section

Collection and Reduction of the Intensity Data. A sample of $(C_6H_5NO)_2PdCl_2$ was prepared by the method of Balch and Petridis.[1] Suitable single crystals could be prepared by slow cooling of a CH_2Cl_2 solution obtained by Soxhlet extraction of the sparingly soluble crude product. Preliminary precession photographs ($hk0$, $hk1$, $h0l$, $h1l$) displayed $2/m$ symmetry with systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) consistent with space group $P2_1/c$. Lattice parameters were obtained by least-squares refinement[17] of the setting angles of 17 reflections with $2\theta \geqslant 21°$ which had been accurately centered on a Picker four-circle X-ray diffractometer. The unit cell constants (23°, λ(Mo Kα_1) 0.70926 Å) obtained in this manner are $a = 5.782$ (4), $b = 14.657$ (9), $c = 8.118$ (5) Å, and $\beta = 138.84$ (3)°. The numbers in parentheses are the standard deviations obtained from the least-squares refinement of the setting angles. Observed (flotation in aqueous $ZnBr_2$) and calculated ($Z = 2$) densities are 1.84 (2) and 1.90 g/cm^3, respectively.

Intensity data were collected from a well-formed, blue-black crystal of dimensions 0.13 × 0.23 × 0.44 mm mounted on a glass fiber with its longest dimension (the crystallographic [100] direction) parallel to the fiber axis. The 0.13-mm dimension was perpendicular to the well developed $\{01\bar{1}\}$ faces; other bounding planes belonged to the $\{011\}$ and $\{100\}$ forms. Narrow-source open-counter ω scans of several reflections showed an average full width of 0.12° at half-maximum, indicative of low mosaic spread. The data were collected on a Picker automatic diffractometer by use of procedures previously described.[18] A takeoff angle of 1.55° was employed. The diffracted beam was filtered through 3.0-mil Nb foil. The counter aperature was 5 mm^2 and was positioned 28 cm from the crystal. The pulse height analyzer was set to admit ~95%

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(17) Programs employed in this structural analysis included local versions of PICK (J. A. Ibers) for cell refinement and generation of diffractometer settings; PICKOUT (R. J. Doedens, J. A. Ibers) for data processing; GONO (W. C. Hamilton) for absorption correction; FORDAP (A. Zalkin) for Fourier summation; UCIGLS (derived from Busing, Martin, and Levy's ORFLS) for structure factor calculations and least-squares refinement; ORFFE (Busing, Martin, and Levy) for function and error calculations; PLANET (D. L. Smith) for least-squares plane calculations; DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson) for preparation of figures; and RSCAN (R. J. Doedens) for evaluation of the weighting scheme. All computations were carried out on the local PDP-10 computer.

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Table I. Atomic Positional and Thermal Parameters for $(C_6H_5NO)_2PdCl_2$ [a]

Atom	x	y	z	β_{11} [b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0	0	0	2119 (9)	242 (1)	1256 (5)	−30 (2)	327 (4)	−25 (1)
Cl	0.26319 (10)	−0.03932 (4)	0.21391 (8)	3334 (20)	357 (3)	1644 (10)	81 (6)	−208 (11)	−7 (5)
O	−0.1777 (3)	0.1402 (1)	0.1845 (3)	3200 (59)	420 (9)	1937 (36)	6 (18)	1106 (38)	−133 (14)
N	−0.0271 (3)	0.1252 (1)	0.0926 (2)	2178 (52)	288 (8)	1287 (30)	32 (16)	236 (32)	−42 (13)
C(1)	0.1132 (4)	0.1987 (1)	0.0484 (3)	2224 (62)	261 (8)	1175 (33)	−2 (18)	−41 (35)	−28 (13)
C(2)	0.0541 (4)	0.2889 (2)	0.0843 (3)	2646 (70)	317 (10)	1493 (40)	92 (21)	9 (42)	−55 (17)
C(3)	0.1961 (5)	0.3577 (2)	0.0369 (4)	3894 (98)	278 (10)	1943 (52)	21 (24)	−288 (57)	−24 (18)
C(4)	0.3940 (5)	0.3381 (2)	−0.0417 (4)	3267 (87)	354 (10)	1722 (46)	−252 (25)	−85 (52)	139 (18)
C(5)	0.4521 (4)	0.2489 (2)	−0.0754 (3)	2611 (67)	423 (12)	1626 (44)	−129 (24)	205 (44)	78 (19)
C(6)	0.3110 (4)	0.1780 (2)	−0.0315 (3)	2440 (69)	312 (10)	1410 (37)	−18 (20)	249 (40)	−16 (16)
H(2) [c]	−0.0877	0.3028	0.1430	4.5 [d]					
H(3)	0.1558	0.4226	0.0594	5.3					
H(4)	0.4962	0.3890	−0.0746	5.1					
H(5)	0.5964	0.2355	−0.1317	4.4					
H(6)	0.3506	0.1134	−0.0566	4.7					

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Tabulated β values are $\times 10^5$. [c] Numbers of hydrogen atoms correspond to those of the carbon atoms to which they are bound. [d] Hydrogen atoms were assigned temperature factors 1 unit greater than the final isotropic B value of the corresponding carbon atom.

of the Mo Kα peak. Data were collected by the θ–2θ scan method. A symmetric scan range of ±0.65° in 2θ from the calculated scattering angle was employed; for reflections with $2\theta > 30°$ an additional 0.05° was added to each end of this range. The intensities of all independent reflections with $2\theta \leqslant 58°$ were measured. The scan rate was 1°/min and stationary-background counts of 20 sec were taken at each end of the scan range. Copper foil attenuators were automatically inserted whenever the count rate exceeded ~10,000 counts/sec; a total of 18 reflections required attenuation. Three standard reflections, chosen to lie in widely separated regions of reciprocal space, were monitored regularly. During the data collection there was no appreciable (<1%) change in the intensities of these standards.

Previously described methods were employed in processing the data.[18] The p factor in the expression for the standard deviation of the observed intensities were assigned a value of 0.05. Of the 1850 independent intensities collected, 1601 were above background by three or more standard deviations. An absorption correction was applied based on a linear absorption coefficient of 17.66 cm^{-1}; the calculated transmission factors ranged from 0.621 to 0.806.

Solution and Refinement of the Structure. The presence of two molecules per cell in space group $P2_1/c$ requires the palladium atom to be situated on a center of symmetry. Hence the atomic coordinates of the nine other nonhydrogen atoms were obtained directly from a three-dimensional Patterson map, complicated only by the presence of superimposed images of the nitrosobenzene ligands. Least-squares refinement of the positional and isotropic thermal parameters for all nonhydrogen atoms based upon the 1601 data with $F_o^2 \geqslant 3\sigma(F_o^2)$ converged to discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.081$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.122$. In this and subsequent refinements, the hydrogen atoms were included as fixed contributions to F_c based upon their "ideal" trigonal position with C–H = 1.0 Å. Further refinement employed anisotropic thermal parameters for all nonhydrogen atoms and converged to final R factors $R_1 = 0.024$ and $R_2 = 0.037$. In the final cycle of refinement, the largest shift of a positional parameter was 0.33σ.

Throughout the least-squares refinement, the weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The final standard deviation of an observation of unit of weight was 1.25. Calculation of $w(\Delta F)^2$ for subsets of the data as a function of uncorrected intensity, observed F, and Bragg angle showed no significant trends; thus confirming that the relative weights were appropriate. Calculation of structure factors for data with $F_o^2 \leqslant 3\sigma(F_o^2)$ revealed six reflections with $|F_o - F_c|/\sigma(F_o) \geqslant 3$; only one of these had $\Delta F/\sigma > 4$. Scattering factors for C, N, and O were taken from ref 19; those of Cromer and Waber[20] were used for Pd and Cl, and those of Stewart, *et al.*,[21] were employed for H. The $\Delta f'$ and $\Delta f''$ values of Cromer[22] were used in correcting for the real and imaginary parts of anomalous scattering by the Pd and Cl atoms.

Final atomic positional and thermal parameters are listed in Table I; bond distances and angles are tabulated in Table II. Table III lists root-mean-square amplitudes of thermal motion and results of least-squares plane calculations are summarized in Table IV. A table of observed and calculated structure factors is available.[23]

Description and Discussion of the Structure

The crystal structure of dichlorobis(nitrosobenzene)-palladium(II) is made up of well-separated monomeric molecules. Two views of the molecular structure are shown in Figures 1 and 2. The space group symmetry requires the metal atom to be located on a center of symmetry, which (in the absence of disorder) requires a trans configuration about the Pd and binding of the nitrosobenzene ligand in its monomeric form. The coordination about the metal ion is square planar, with a Cl-Pd-N angle of 90.70 (6)°. Coordination of the nitrosobenzene is solely through its nitrogen atom. The molecule possesses no symmetry elements beyond the crystallographically imposed center of symmetry; but for a twisting of the phenyl rings about the C-N bonds (*vide infra*) the molecular symmetry would be C_{2h}-$2/m$.

The Pd-Cl distance of 2.295 (1) Å is comparable to the value of 2.287 (2) Å observed in *trans*-dichlorobis(dimethyl sulfoxide)palladium(II).[24] These are "normal" Pd-Cl bond distances;[25] longer distances are generally observed in *cis*-dichloropalladium complexes.[26] The Pd-N distance of 1.994 (2) Å is likewise of the expected magnitude. Representative Pd-N(sp^2) distances with which it might be compared include 1.961 (11) Å in bis(salicylaldoximato)palladium(II),[27] 1.984 (8) Å for the Pd-NO_2 distance in $[Pd(NO_2)(NH_3)_3]^+$,[28] 2.022 (9) Å in bis(2,2′-dipyridyliminato)palladium(II),[29] and 2.03

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Table II. Bond Distances (Å) and Angles (deg)

	(a) Distances		
Pd-Cl	2.295 (1)	N-O	1.209 (3)
Pd-N	1.994 (2)	N-C(1)	1.411 (3)
C(1)-C(2)	1.402 (3)	C(4)-C(5)	1.383 (4)
C(2)-C(3)	1.373 (4)	C(5)-C(6)	1.384 (4)
C(3)-C(4)	1.381 (4)	C(6)-C(1)	1.309 (3)
Mean C-C	1.385 (10)[a]		
	(b) Angles		
N-Pd-Cl	90.70 (6)	Pd-N-C(1)	122.9 (1)
Pd-N-O	118.7 (2)	O-N-C(1)	118.2 (2)
N-C(1)-C(2)	120.9 (2)	N-C(1)-C(6)	117.5 (2)
C(2)-C(1)-C(6)	121.6 (2)	C(3)-C(4)-C(5)	120.6 (2)
C(1)-C(2)-C(3)	118.3 (2)	C(4)-C(5)-C(6)	120.1 (2)
C(2)-C(3)-C(4)	120.7 (2)	C(5)-C(6)-C(1)	118.6 (2)
Mean C-C-C	120.0 (13)		

[a] The figure in parentheses following mean values in this table is the standard deviation of an *individual* distance or angle as estimated by $S = \{[1/(n-1)]\Sigma_{i=1}^{n} (\bar{x} - x_i)^2\}^{1/2}$ where x_i is an individual measurement and $\bar{x}$ is the mean value of the n measurements of presumably equivalent quantities.

Table III. Principal Root-Mean-Square Amplitudes of Thermal Motion (Å)

Atom	Shortest	Intermediate	Longest
Pd	0.1615 (4)	0.1806 (4)	0.2103 (4)
Cl	0.1952 (18)	0.2175 (7)	0.2560 (8)
O	0.181 (2)	0.217 (2)	0.284 (2)
N	0.174 (2)	0.191 (2)	0.209 (2)
C(1)	0.168 (3)	0.186 (3)	0.206 (3)
C(2)	0.181 (3)	0.209 (3)	0.230 (3)
C(3)	0.174 (3)	0.233 (3)	0.279 (4)
C(4)	0.178 (3)	0.225 (3)	0.263 (3)
C(5)	0.195 (3)	0.222 (3)	0.238 (3)
C(6)	0.184 (3)	0.200 (3)	0.218 (3)

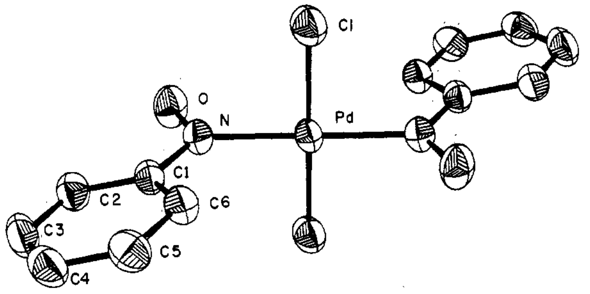

Figure 1. A perspective view of the structure of $(C_6H_5NO)_2PdCl_2$. Thermal ellipsoids are drawn at the 50% probability level.

(1) Å in a dipyrromethene-palladium(II) complex.[30]

The bond angles about the nitrogen atom are all within less than 3° of their ideal trigonal value of 120°. The N-O and N-C distances are 1.209 (3) and 1.411 (3) Å, respectively. No detailed structural data are available for nitrosobenzene itself and crystal structure analyses of dimeric *p*-bromonitrosobenzene,[31] dimeric tribromonitrosobenzene,[32] and monomeric *p*-iodonitrosobenzene[33] were based upon two-dimensional data. Among other $(RNO)_2$ compounds of known structure,[34] the most precise molecular parameters are available for 2-nitronitrosoethane[35] and for nitrosocyclohexane.[36] These two compounds display N-O distances of 1.262 (3) and 1.272 (6) Å, respectively, values which are consistent with a bond order between 1 and 2.[34] The shorter distance we observe is of reasonable magnitude for an N=O double bond. As expected, the N-C distance of 1.411 Å is less than the corresponding distances of 1.470 (4) and 1.488 (6) Å in 2-nitronitrosoethane and nitrosocyclohexane, respectively. The bond distances within the phenyl ring have a mean value of 1.385 Å. The standard deviation of a phenyl C-C distance, as estimated from the variation of the individual distances, is 0.010 Å. The fact that this estimate is greater than the least-squares standard deviations suggests that the latter may be somewhat underestimated. The largest departure from the expected C-C distances is the C(2)-C(3) distance. The C-C-C angles within the phenyl ring average to 120.0° and the six ring carbon atoms are accurately coplanar.

As is clearly evident in Figure 2, the nitrosobenzene ligand is nonplanar, owing to a twisting of the phenyl ring about the N-C bond. The magnitude of the twist, as measured by the dihedral angle between the ring plane and the C(1)-N-O plane, is 11.8°. A similar nonplanarity was noted in the *p*-bromonitrosobenzene dimer,[31] though monomeric *p*-iodonitrosobenzene was reported to be planar. Similar torsion

Table IV.

Molecular Planes[a]

1. Plane containing Pd, Cl, and N
   Equation of plane: $0.7891X + 0.3086Y - 0.5311Z = 0.0000$
2. Plane containing Pd, O, and C(1)
   Equation of plane: $-0.5935X + 0.2310Y - 0.7710Z = 0.0000$
   Distance to plane (Å)
   N −0.028
3. Plane containing C(1), C(2), C(3), C(4), C(5), C(6), and N
   Equation of plane: $-0.4610X + 0.0631Y - 0.8851Z = -0.4510$
   Distances to plane (Å)

C(1)	0.0001	C(5)	−0.0046
C(2)	−0.0066	C(6)	0.0033
C(3)	0.0054	N	0.0014
C(4)	0.0009		

Dihedral Angles between These Planes

Planes	Angle, deg
1-2	89.1
1-3	82.8
2-3	13.9

[a] Unit weights were employed in the calculation of plane 3. Equations of planes are expressed with respect to coordinates (*X*, *Y*, *Z*) referred to an orthogonal system (*A*, *B*, *C*) oriented with *A* along *a*, *B* along *b*, and *C* in the direction of *A* × *B*.

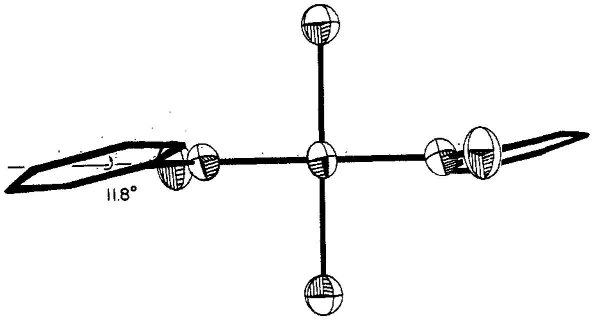

Figure 2. A schematic diagram of the molecular structure, as viewed along a direction perpendicular to the coordination plane. The angle shown is the dihedral angle between the plane of the phenyl ring and the C(1)-N-O plane.

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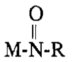
angles are found, for example, in the coordinated phenyldiazonium cation of $HB(C_3N_2H_3)_3Mo(CO)_2N_2C_6H_5$ (~20°)[37] and *trans*-azobenzene (~17°).[38] The nonbonded contact between the hydrogen atom bound to carbon atom 5 and the nitrosyl oxygen atom is 2.75 Å in length. Examination of molecular models shows that approach of additional ligands perpendicular to the coordination plane is effectively blocked by the phenyl ring, in particular by the hydrogen atom bound to C(6). This hydrogen atom makes an estimated 2.69-Å nonbonded contact with the Pd atom.

The monodentate coordination of the nitrosobenzene contrasts with the involvement of both N and O atoms in metal coordination in bis[tricarbonyl(3-chloro-2-methylnitrosobenzene)iron].[5] The configuration of the bonded RNO group in the iron dimer differs substantially from that which we observe. The principal variations are a longer N-O distance of 1.40 (1) Å, a smaller C-N-O angle of 112.2 (7)°, and a greater torsional angle (20.2°) about the N-C bond. The distinction between N and O bonding in metal-RNO complexes has in general been difficult to draw. This difficulty stems in part from uncertainty as to the assignment of vibrational spectra of the aromatic nitroso compounds themselves.[39,40] O bonding has been favored in some instances[9,10] and could well prevail in complexes of "hard" metal ions. Authentic examples of O-bonded arylnitroso ligands would be useful in formulating spectroscopic criteria for distinguishing between the various bonding possibilities.

Demonstration of this mode of metal coordination for nitrosobenzene gives rise to the interesting question of whether this type of



$$\overset{\displaystyle O}{\overset{\|}{\text{M-N-R}}}$$

linkage could be obtained by nucleophilic attack on a coordinated nitrosyl group or by a nitrosyl insertion reaction, analogous to the well-known reactions of metal-coordinated carbonyl groups. Nucleophilic attack of hydroxide[15b] or methoxide[16] ion on coordinated NO is known, as are a few reactions in which NO is inserted into a metal-carbon bond.[41,42] However, to date these reactions have not been shown to yield simple metal-arylnitroso complexes of the sort found here.

Registry No. *trans*-$(C_6H_5NO)_2PdCl_2$, 37680-12-9.

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Addition of Ethanethiol to Coordinated Isocyanides. Structure of *trans*-Bis(methyl isocyanide)bis(methylamino(thioethoxy)carbene)platinum(II) Hexafluorophosphate, $[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2CH_3)\}_2][PF_6]_2$

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The structure of *trans*-bis(methyl isocyanide)bis(methylamino(thioethoxy)carbene)platinum(II) hexafluorophosphate, $[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2CH_3)\}_2][PF_6]_2$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a cell of dimensions a = 8.913 (6), b = 10.526 (6), and c = 7.750 (5) Å with α = 94.77 (3), β = 88.30 (3), and γ = 117.20 (3)°. The observed and calculated densities are 1.98 (2) and 1.980 (1) g/cm³, respectively. Full-matrix least-squares refinement has resulted in R = 0.039 for the 2198 data with $F_o^2 \geqslant 3\sigma(F_o^2)$. The coordination about the Pt atom is square planar and the cation is required to have $\bar{1}$-C_i symmetry. The Pt-C(carbene) distance is 2.058 (7) Å and the Pt-$CNCH_3$ distance is 1.968 (9) Å. The C-N and C-S distances of the carbene ligand are 1.30 (1) and 1.681 (8) Å, respectively. The structural trans influence of carbene ligands is shown to be similar to that of phosphine ligands.

Introduction

A number of metal "carbene"[1,2] complexes resulting from addition reactions of coordinated isocyanide ligands have been structurally characterized by single-crystal X-ray diffraction.[3-8] Several of these complexes[4-8] involve chelative addition to two cis isocyanide ligands to give "dicarbene" com-

[1] "Carbene" nomenclature has become generally used for C(R)R′ ligands derived from reactions of coordinated carbonyls and isocyanides. Since extensive electron delocalization is possible in these ligands, they are not simple carbenes but fall into the category of resonance-stabilized carbenes.[2]

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