Inorg. Chem. 1981, 20, 1534-1538

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Structure of *trans*-$[RhCl(CO)(Ph_2AsCH_2AsPh_2)]_2 \cdot CH_2Cl_2$: A Complex Showing a Significant Rh–Rh Shortening Relative to That of the Unsolvated Analogue

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Received September 8, 1980

The structure of *trans*-$[RhCl(CO)(Ph_2AsCH_2AsPh_2)]_2 \cdot CH_2Cl_2$ has been determined by X-ray crystallography and is found to consist of two square-planar rhodium centers bridged by two transoid diarsine ligands. These square planes are eclipsed and mutually parallel but are inclined to the Rh–Rh vector by 83.7°. Each rhodium atom has two trans arsine groups and trans chloro and carbonyl ligands. The Rh–Rh separation, at 3.236 (2) Å, is significantly shorter than that observed in the unsolvated analogue, in which the metals are 3.396 (1) Å apart, and is even shorter than the present intraligand As–As distance of 3.272 (2) Å. The Rh–Rh compression in the present unsolvated complex results from packing considerations since the methylene chloride of solvation lies directly along the Rh–Rh axis in the lattice. The complex crystallizes in the space group $P2_1/c$ with $a = 12.257$ (3) Å, $b = 15.868$ (3) Å, $c = 13.469$ (3) Å, $\beta = 95.19$ (2)°, and $Z = 2$. On the basis of 2738 unique reflections the structure was refined by full-matrix, least-squares techniques to $R = 0.058$ and $R_w = 0.071$.

Introduction

A recent development in metal carbonyl chemistry is the structural characterization of ketonic carbonyl ligands[1-3] (i.e., bridging carbonyls which are not accompanied by metal–metal bonds) in three binuclear DPM and DAM complexes (DPM = $Ph_2PCH_2PPh_2$, DAM = $Ph_2AsCH_2AsPh_2$). In all previous determinations the bridging carbonyl ligands were always accompanied by metal–metal bonds.[4] Since all three structures involving this new carbonyl bonding mode have accompanying bridging DPM or DAM ligands, it seems probable that the stabilities of these unusual species are due in a large part to the DPM and DAM ligands which allow the metals the required separation for optimum bonding with the ketonic carbonyl groups.

Although the DPM and DAM ligands are extremely similar, significant differences are observed in the stabilities of ketonic carbonyl complexes with each of these accompanying diphosphine or diarsine groups. With Pd[1] and Pt[2] the ketonic carbonyl complexes of DAM are more stable than those of DPM, whereas the opposite seems to be true of Rh.[5] The obvious difference in these ligands lies in their bite sizes; the DAM group, which bonds to the metals via As atoms, is capable of bridging larger distances than the DPM group having the smaller P atom. Therefore, the DAM ligand should tend to favor larger metal–metal separations. In complexes containing ketonic carbonyl ligands we might expect that the stabilities of these species would be very dependent on the preferred metal–metal separations and therefore on the accompanying bridging groups (i.e., DPM or DAM). It is of interest therefore, to obtain information on the effects of bridging diphosphines and diarsines on the preferred metal–metal separations in order to gain a better understanding of the factors favoring the unusual ketonic carbonyl ligand. The structure of the methylene chloride solvate of *trans*-$[RhCl(CO)(DAM)]_2$, which is reported herein, is useful in this regard since it presents an interesting comparison with the unsolvated complex[6] and with the analogous unsolvated DPM analogue[7] and therefore gives a valuable indication about the factors affecting the metal–metal separations in these binuclear species.

Table I. Summary of Crystal Data and Intensity Collection

comp	*trans*-$[RhCl(CO)(DAM)]_2 \cdot CH_2Cl_2$
fw	1362.26
formula	$C_{52}H_{44}As_4Cl_2O_2Rh_2 \cdot CH_2Cl_2$
cell parameters	
a	12.257 (3) Å
b	15.868 (3) Å
c	13.469 (3) Å
β	95.19 (2)°
V	2608.9 Å^3
Z	2
density	1.734 g cm^{-3} (calcd); 1.728(6) g cm^{-3} (obsd)
space group	$P2_1/c$
cryst dimensions	0.436 × 0.431 × 0.368 mm
cryst shape	monoclinic prism with faces of the form {021}, {011}, {100}, {01$\bar{2}$}
cryst vol	0.0344 mm^3
temp	20 °C
radiation	Cu Kα
μ	103.284 cm^{-1}
range in abs cor factors	0.068–0.200
receiving aperture	6 × 6 mm
takeoff angle	4.4°
scan speed	2° min^{-1}
scan range	1.0° below Kα_1 to 1.0° above Kα_2
bkgd counts	10 s ($3° \leqslant 2\theta \leqslant 65°$) 20 s ($65° \leqslant 2\theta \leqslant 95°$) 40 s ($95° \leqslant 2\theta \leqslant 120°$)
2θ limits	3–120°
unique data used ($F_o^2 > 3\sigma(F_o^2)$)	2738
final no. of parameters	136
error in observn of unit wt	1.926
R	0.058
R_w	0.071

Experimental Section

All solvents were appropriately dried and degassed prior to use, and all reactions were carried out under an atmosphere of dinitrogen. *trans*-$[RhCl(CO)(DAM)]_2$ was prepared by the reported method.[8] Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrometer, with use of Nujol mulls on KBr plates.

Data Collection. Dark red prismatic crystals of *trans*-$[RhCl(CO)(DAM)]_2$ as the methylene chloride solvate were obtained from the reaction of the unsolvated complex with CS_2 in CH_2Cl_2 solution followed by slow diethyl ether diffusion and cooling. One of these

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(1) (a) Colton, R.; McCormick, M. J.; Pannan, C. D. *J. Chem. Soc., Chem. Commun.* **1977**, 823. (b) Colton, R.; McCormick, M. J.; Pannan, C. D. *Aust. J. Chem.* **1978**, *31*, 1425.

(2) Brown, M. P.; Keith, A. N.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chim. Acta* **1979**, *34*, L223.

(3) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* **1980**, *193*, C46.

(4) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

(5) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 209.

(6) Mague, J. T. *Inorg. Chem.* **1969**, *8*, 1975.

(7) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.

(8) Mague, J. T.; Mitchner, J. P. *Inorg. Chem.* **1969**, *8*, 119.

0020-1669/81/1320-1534$01.25/0

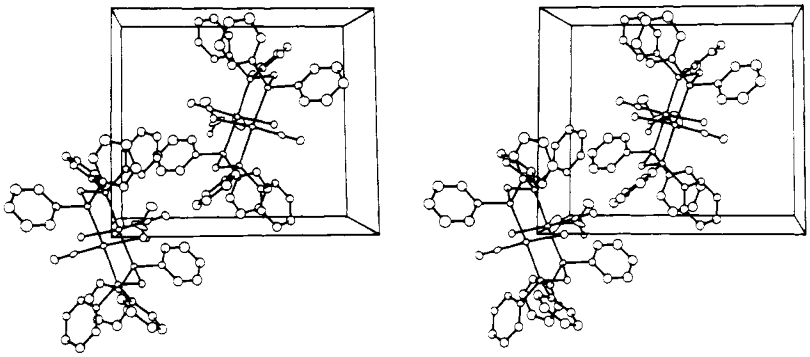

Figure 1. Stereoview of the unit cell of *trans*-[RhCl(CO)(DAM)]$_2$·CH$_2$Cl$_2$. The *y* axis is horizontal to the right, the *z* axis runs from top to bottom, and the *x* axis goes into the page; 20% thermal ellipsoids are used on this and all subsequent drawings except for methylene hydrogen atoms which are drawn artifically small. Only one set of disordered dichloromethane atoms is shown.

crystals was mounted and sealed in a glass capillary tube. Preliminary film data showed that the crystal belonged to the monoclinic system with extinctions (*h*0*l*, *l* odd; 0*k*0, *k* odd) characteristic of the centrosymmetric space group $P2_1/c$. Accurate cell parameters were obtained by a least-squares analysis of 12 carefully centered reflections chosen from diverse regions of reciprocal space (60° ≤ 2θ ≤70°, Cu Kα radiation) and obtained with use of a narrow X-ray source. The widths at half-height of several strong reflections (ω scan, open counter) lay in the range 0.15–0.20° (see Table I for pertinent crystal data).

Data were collected on a Picker four-circle automated diffractometer equipped with a scintillation counter and pulse height analyzer, tuned to accept 90% of the Cu Kα peak. Background counts were measured at both ends of the scan range with stationary crystal and counter. The intensities of three standard reflections were measured every 100 reflections, and four additional standards were measured three times a day. All standards remained constant to within 1% of the mean throughout data collection.

The intensities of 4068 unique reflections were measured with use of Cu Kα radiation. Data were processed in the usual manner using a value of 0.05 for *p*.[9] Absorption corrections were applied to the data using Gaussian integration.[10]

Structure Solution and Refinement. The position of the independent Rh atom was obtained from a sharpened Patterson synthesis. Subsequent refinements and difference Fourier calculations led to the location of all other atoms. Atomic scattering factors were taken from Cromer and Waber's tabulation[11] for all atoms except hydrogen for which the values of Stewart et al.[12] were used. Anomalous dispersion terms[13] for Rh, As, and Cl were included in F_c. All carbon atoms of the phenyl rings were refined as rigid groups having D_{6h} symmetry and C–C distances of 1.392 Å. The hydrogen atoms were included as fixed contributions and were not refined. Their idealized positions were calculated from the geometries about their attached carbon atoms by using C–H distances of 0.95 Å. Hydrogen atoms were assigned isotropic thermal parameters of 1 Å^2 greater than those of their attached isotropic carbon atom or 1 Å^2 greater than the equivalent isotropic *B* of an anisotropic carbon atom. All other nongroup atoms were refined individually with anisotropic thermal parameters. The dichloromethane solvent molecule is disordered such that one chlorine atom is located on the 2(b) inversion center and the other chlorine atom and the methylene group are inversion disordered about this point.

The final model, with 136 parameters varied, converged to R = 0.058 and R_w = 0.071.[14] In the final difference Fourier map the 20 highest peaks were in the vicinity of the metals and in the regions about the phenyl rings and the disordered solvent molecule (1.19–0.49 e/Å^3). A typical carbon atom in earlier syntheses had an electron density of about 4.9 e/Å^3. The final positional parameters of the group

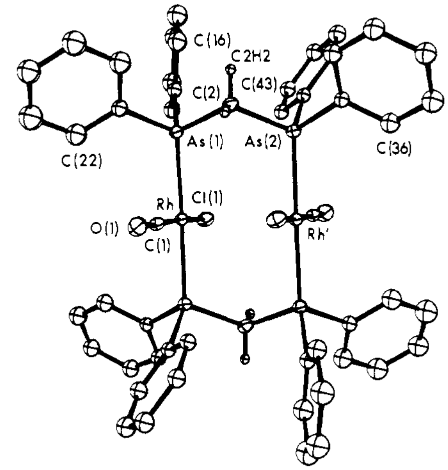

Figure 2. Perspective view of *trans*-[RhCl(CO)(DAM)]$_2$ showing the numbering scheme. The numbering on the phenyl carbon atoms starts at the carbon bonded to phosphorus and increases sequentially around the ring.

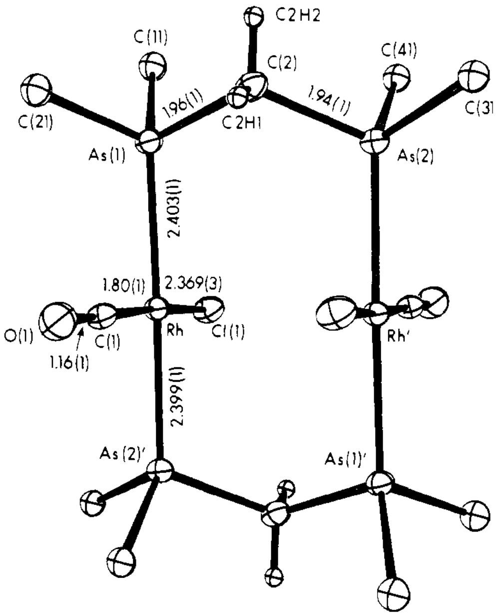

Figure 3. Inner coordination sphere of *trans*-[RhCl(CO)(DAM)]$_2$ showing some relevant bond lengths. Only the first carbon atom of each phenyl ring is shown. In addition, the Rh–Rh' separation is 3.236 (2) Å and As(1)–As(2) = 3.272 (2) Å.

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(9) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(10) Besides local programs, the following were used in the solution and refinement of the structure: FORDAP, the Fourier summation program by A. Zalkin; SFLS-5, structure factor and least-squares refinement by C. J. Prewitt; ORFFE, program for calculating bond lengths, angles, and associated standard deviations by W. Busing and H. A. Levy; ORTEP, plotting program by C. K. Johnson; AGNOST, the Northwestern University absorption program which includes the Coppens–Leiserowitz–Rabinovich logic for Gaussian integration.

(11) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(13) Cromer, D. T. and Liberman, D. J. *J. Chem. Phys.*, **1970**, *53*, 3175.

(14) $R = \sum||F_o| - |F_c|| / \sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of *trans*-[RhCl(CO)(DAM)]$_2$·CH$_2$Cl$_2$

Atom	x[a]	y	z	U11[b]	U22	U33	U12	U13	U23
Rh	0.12437(6)	0.02224(5)	-0.02197(5)	4.36(5)	3.37(4)	2.94(4)	-0.22(3)	-0.15(3)	-0.19(3)
As(1)	0.16601(9)	0.07691(7)	0.14570(8)	4.54(6)	4.00(6)	3.30(5)	-0.35(5)	-0.25(4)	-0.41(5)
As(2)	-0.08369(9)	0.02606(7)	0.19001(7)	4.50(7)	3.63(6)	3.15(6)	-0.10(5)	-0.13(5)	-0.17(5)
Cl(1)	0.1612(2)	-0.1218(2)	0.0132(2)	6.9(2)	4.2(1)	4.6(1)	0.4(1)	-0.9(1)	0.0(1)
Cl(2)	1/2	0	0	19(1)	15.0(9)	31(2)	2.2(8)	-12(1)	-8(1)
Cl(3)	0.4960(7)	0.1382(7)	-0.0961(6)	9.4(6)	17(1)	8.1(6)	0.7(6)	1.7(5)	1.9(6)
O(1)	0.0960(8)	0.2007(5)	-0.0828(6)	11.1(8)	3.9(5)	5.6(5)	-0.0(5)	0.2(5)	0.3(4)
C(1)	0.1048(9)	0.1305(7)	-0.0586(7)	5.1(6)	5.2(7)	3.5(5)	-1.4(6)	0.4(4)	-1.4(5)
C(2)	0.0317(9)	0.1098(7)	0.2036(8)	4.9(6)	4.5(6)	4.1(6)	-0.2(5)	-1.0(5)	0.2(5)
C(3)	0.549(3)	0.089(4)	-0.001(2)	7(2)	29(6)	9(2)	2(3)	1(2)	13(3)

[a] Estimated standard deviations in the least signicant figure(s) are given in parentheses in this and all subsequent tables.

[b] The form of the thermal ellipsoid is: $\exp[-2*PI^2(a^{*2}U11h^2+b^{*2}U22k^2+c^{*2}U33l^2+2a*b*U12hk+2a*c*U13hl+2b*c*U23kl)]$. The quantities given in the table are the thermal coefficients x 10^2.

Table III

Derived Parameters for the Rigid-Group Atoms of *trans*-[RhCl(CO)(DAM)]$_2$·CH$_2$Cl$_2$

Atom	x	y	z	$B(A^2)$	Atom	x	y	z	$B(A^2)$
C(11)	0.2491(9)	0.0177(6)	0.2543(6)	3.7(2)	C(31)	-0.2049(6)	0.0832(5)	0.2445(6)	3.2(2)
C(12)	0.2987(9)	-0.0588(6)	0.2352(6)	4.9(3)	C(32)	-0.1927(6)	0.1526(5)	0.3077(5)	4.5(2)
C(13)	0.3559(8)	-0.1029(5)	0.3127(8)	6.8(4)	C(33)	-0.2840(8)	0.1884(5)	0.3454(6)	5.4(3)
C(14)	0.3635(9)	-0.0706(6)	0.4091(6)	6.8(3)	C(34)	-0.3877(6)	0.1548(5)	0.3198(6)	5.5(3)
C(15)	0.3139(9)	0.0060(6)	0.4281(6)	7.5(4)	C(35)	-0.4000(6)	0.0854(5)	0.2566(5)	6.0(3)
C(16)	0.2567(8)	0.0501(5)	0.3507(8)	6.0(3)	C(36)	-0.3086(8)	0.0496(5)	0.2189(6)	5.1(3)
C(21)	0.2434(7)	0.1829(5)	0.1505(7)	3.8(2)	C(41)	-0.0362(7)	-0.0541(5)	0.2939(7)	3.2(2)
C(22)	0.3204(8)	0.1964(6)	0.0823(7)	6.2(3)	C(42)	0.0423(7)	-0.1134(5)	0.2735(4)	3.7(2)
C(23)	0.3802(6)	0.2711(6)	0.0851(5)	8.3(4)	C(43)	0.0793(6)	-0.1720(5)	0.3458(6)	4.4(2)
C(24)	0.3631(7)	0.3322(5)	0.1563(7)	7.1(4)	C(44)	0.0377(7)	-0.1712(5)	0.4387(7)	5.0(3)
C(25)	0.2861(8)	0.3186(6)	0.2245(7)	7.5(4)	C(45)	-0.0409(7)	-0.1118(5)	0.4591(4)	5.4(3)
C(26)	0.2263(6)	0.2440(6)	0.2216(5)	6.2(3)	C(46)	-0.0779(6)	-0.0533(5)	0.3867(6)	4.6(2)

Rigid-Group Parameters

	Xc[a]	Yc	Zc	Delta[b]	Epsilon	Eta
Ring1	0.3063(5)	-0.0264(4)	0.3317(5)	2.638(6)	1.863(6)	5.671(6)
Ring2	0.3032(5)	0.2575(4)	0.1534(5)	0.435(6)	0.892(7)	4.360(6)
Ring3	-0.2963(4)	0.1190(3)	0.2822(4)	0.658(5)	0.147(6)	5.741(6)
Ring4	0.0007(4)	-0.1126(3)	0.3663(4)	2.459(5)	1.205(6)	5.248(6)

[a] Xc,Yc and Zc are the fractional coordinates of the centroid of the rigid group.

[b] The rigid group orientation angles Delta,Epsilon and Eta(radians) are the angles by which the rigid body is rotated with respect to a set of axes X,Y and Z. The origin is the centre of the ring; X is parallel to a* , Z is parallel to c and Y is parallel to the line defined by the intersection of the plane containing a* and b* with the plane containing b and c.

and nonhydrogen atoms are given in Table II and III. The derived hydrogen positions and their thermal parameters and a listing of observed and calculated structure factor amplitudes used in the refinement are available.[15]

Description of Structure and Discussion

The unit cell of *trans*-[RhCl(CO)(DAM)]$_2$·CH$_2$Cl$_2$, shown in Figure 1, contains discrete, well-separated dimeric units of the rhodium complex located at the 2(a) inversion centers and disordered methylene chloride of solvation at the 2(b) inversion centers. These CH$_2$Cl$_2$ molecules are located along the Rh–Rh vectors. Figure 2 presents a perspective view of the complex including the numbering scheme (phenyl hydrogens have the same numer as their attached carbon atoms). The inner coordination sphere of the title compound is shown in Figure 3 along with some relevant bond lengths.

The dichloromethane solvent molecule, although disordered, displays the expected geometry with C–Cl bond lengths of 1.54 (6) and 1.59 (3) Å (see Table IV) and a Cl–C–Cl angle of 109 (3)° (Table V). These parameters are not unreasonable considering the disorder of this molecule and compare well with other determinations.[16] The only significant nonbonded contacts involving the CH$_2$Cl$_2$ molecule are between the chlorine atoms and the hydrogen atoms of the DAM phenyl groups at 2.79 Å. All contacts between the methylene chloride molecule and the atoms in the rhodium square plane are greater than 4.25 Å (see Table IV).

The *trans*-[RhCl(CO)(DAM)]$_2$ complex displays essentially the expected geometry, with however some rather unexpected subtle differences between it and the unsolvated DAM[6] and DPM[7] analogues (vide infra). As expected, the coordination about each rhodium atom is effectively square planar (Table VI), having two arsines mutually trans as are the chloro and carbonyl ligands. The dimeric unit is composed of two of these parallel square planes in an eclipsed conformation bridged by the diarsine ligands. These rhodium square planes are ar-

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(15) Supplementary material.

(16) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060. Cowie, M.; Haymore, B. L.; Ibers, J. A. *ibid.* **1975**, *14*, 2617.

Table IV. Selected Distances (Å) in *trans*-$[\mathrm{RhCl(CO)(DAM)}]_2\cdot\mathrm{CH_2Cl_2}$

Bond Distances

Rh-As(1)	2.430 (1)		As(1)-C(11)	1.946 (6)	1.937 (7)
Rh-As(2)′[a]	2.399 (1)		As(1)-C(21)	1.929 (7)	
Rh-Cl(1)	2.370 (3)		As(2)-C(31)	1.941 (5)	
Rh-C(1)	1.80 (1)		As(2)-C(41)	1.941 (5)	
C(1)-O(1)	1.16 (1)		Cl(2)-C(3)	1.54 (6)	1.56 (6)
As(1)-C(2)	1.96 (1)	1.95 (1)[b]	Cl(3)-C(3)	1.59 (3)	
As(2)-C(2)	1.94 (1)				

Nonbonded Distances

Rh-Rh′	3.236 (2)	O(1)-H(26)[e]	2.52	Cl(3)-H(22)	2.79
As(1)-As(2)	3.272 (2)	O(1)-H(44)[f]	2.80	Cl(1)-Cl(2)	4.598 (3)
Cl(1)-H(12)	2.62	O(1)-H(42)′	2.90	Cl(2)-Rh	4.600 (1)
Cl(1)-H(33)[c]	2.91	C(1)-H(42)′	2.84	Cl(3)-Cl(1)[g]	4.256 (9)
Cl(1)-H(44)[d]	2.91	C(1)-H(22)	2.98	Cl(3)-C(1)	4.87 (1)
Cl(1)-H(42)	2.97				

[a] Primed atoms are related to unprimed ones by a center of inversion at the origin in this and all subsequent tables. [b] For averaged quantities the estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean. [c] Related by $\bar{x}, -{}^1\!/_2 + y, {}^1\!/_2 - z$. [d] Related by $x, -{}^1\!/_2 - y, -{}^1\!/_2 + z$. [e] Related by $x, {}^1\!/_2 - y, -{}^1\!/_2 + z$. [f] Related by $\bar{x}, {}^1\!/_2 + y, {}^1\!/_2 - z$. [g] Related by $1 - x, \bar{y}, \bar{z}$.

Table V. Selected Angles (Deg) in *trans*-$[\mathrm{RhCl(CO)(DAM)}]_2\cdot\mathrm{CH_2Cl_2}$

Bond Angles

As(1)-Rh-As(2)	177.69 (5)	Rh-As(1)-C(21)	113.8 (3)	C(31)-As(2)-C(41)	102.9 (3)
As(1)-Rh-Cl(1)	97.97 (7)	Rh-As(2)′-C(31)′	113.9 (2)	As(1)-C(11)-C(12)	119.4 (5)
As(1)-Rh-C(1)	85.7 (3)	Rh-As(2)′-C(41)′	119.6 (2)	As(1)-C(11)-C(16)	120.6 (5)
As(2)′-Rh-Cl(1)	84.25 (7)	Cl(2)-C(3)-Cl(3)	109 (3)	As(1)-C(21)-C(22)	118.2 (5)
As(2)′-Rh-C(1)	92.0 (3)	As(1)-C(2)-As(2)	114.4 (5)	As(1)-C(21)-C(26)	121.7 (5)
Cl(1)-Rh-C(1)	174.4 (3)	C(2)-As(1)-C(11)	103.4 (4)	As(2)-C(31)-C(32)	123.8 (4)
Rh-C(1)-O(1)	178 (1)	C(2)-As(1)-C(21)	100.6 (4)	As(2)-C(31)-C(36)	116.1 (4)
Rh-As(1)-C(2)	110.6 (3)	C(2)-As(2)-C(31)	102.8 (4)	As(2)-C(41)-C(42)	117.9 (4)
Rh-As(2)′-C(2)′	113.3 (3)	C(2)-As(2)-C(41)	102.3 (4)	As(2)-C(41)-C(46)	122.1 (4)
Rh-As(1)-C(11)	125.3 (2)	C(11)-As(1)-C(21)	100.0 (3)		

Torsion Angles

As(1)-Rh-Rh′-As(2)	2.16 (5)	C(11)-As(1)-As(2)-C(41)	7.8 (3)
Cl(1)-Rh-As(1)-C(11)	17.1 (3)	C(21)-As(1)-As(2)-C(31)	8.6 (5)
Cl(1)-Rh-As(2)′-C(31)′	58.6 (3)	C(11)-As(1)-As(2)′-C(31)′	41.6 (4)
C(1)-Rh-As(1)-C(21)	35.7 (4)	C(21)-As(1)-As(2)′-C(41)′	40.4 (4)
C(1)-Rh-As(2)-C(41)′	5.1 (4)		

Table VI. Least-Squares Plane Calculations[a]

plane no.	equation	plane no.	equation
1	$-0.2785X + 0.9143Y - 0.2942Z - 0.0 = 0.0$	2	$0.9773X + 0.1213Y - 0.1740Z - 1.6185 = 0.0$

	dev from planes, Å							
plane no.	Rh	As(1)	As(2)	As(2)′	Cl(1)	O(1)	C(1)	C(2)
1[c]	−0.0228 (8)	0.024 (1)	−0.022 (1)					0.75 (1)[b]
2	−0.0085 (8)	0.004 (1)		0.004 (1)	0.032 (3)	0.21 (1)	0.09 (1)	

Angle between Planes 1 and 2: −83.7°

[a] X, Y, and Z are orthogonal coordinates (Å) with X along the a axis, Y in the ab plane, and Z along the c^* axis. [b] Not included in plane calculation. [c] Plane 1 has been restricted to pass through the origin.

Table VII. Comparison of the Structural Parameters of *trans*-$[\mathrm{RhCl(CO)(L\text{-}L)}]_2$

	$[\mathrm{RhCl(CO)\text{-}(DPM)}]_2$[a]	$[\mathrm{RhCl(CO)\text{-}(DAM)}]_2$[b]	$[\mathrm{RhCl(CO)\text{-}(DAM)}]_2\cdot\mathrm{CH_2Cl_2}$
Rh-Rh, Å	3.2386 (5)	3.396 (1)	3.236 (2)
Rh-L,[c] Å	2.3141 (9), 2.3315 (9)	2.410 (1), 2.404 (1)	2.399 (1), 2.430 (1)
L-L,[c] Å	3.130 (1)	3.288 (2)	3.272 (2)
L-C-L,[c] Å	116.8 (2)	113.5 (4)	114.4 (5)
C(1)-Rh-Rh′-Cl′, deg	2.66	1.92	3.79
Rh′-Rh-Cl,[d] deg	75.9	68.5	83.7

[a] Reference 7. [b] Reference 6. [c] L = P, As. [d] Approximates the angle between the Rh square plane and Rh-Rh vector.

ranged such that the chloro ligands on adjacent rhodium atoms are mutually trans as are the carbonyl ligands, as demanded by the crystallographically imposed $\bar{1}$ symmetry. However the square planes in the present structure are not perpendicular to the Rh-Rh vector but are inclined to it by ca. 83.7°. Analogous skewing of these planes was observed in the structures of *trans*-$[\mathrm{RhCl(CO)(DAM)}]_2$[6] and *trans*-$[\mathrm{RhCl(CO)(DPM)}]_2$[7] but in these complexes the skewing was more severe at 68.5 and 75.9°, respectively (see Table VII which shows a comparison of structural parameters for these three complexes). In all cases the skewing seems to result from attempts to minimize nonbonded contacts between the equatorial chloro and carbonyl ligands and the phenyl rings of the bridging DAM or DPM ligands. In the present structure two phenyl groups (rings 2 and 3) are particularly successful in avoiding the equatorial ligands, yielding C(21)–As(1)–Rh–C(1) and C(31)–As(2)–Rh′–Cl(1)′ torsion angles of 35.7 (4) and 58.6 (3)°, respectively, whereas rings 1 and 4 have corresponding torsion angles of 17.1 (3) and 5.1 (4)° (Table V), indicating that they are nearly eclipsed with the equatorial ligands. However, as shown in Figure 1, these phenyl rings are twisted such that the ortho hydrogen atoms are directed at the open regions between the equatorial ligands and do not come into close contact with these groups.

Within the Rh–DAM framework the parameters are not unexpected, comparing well with those of the unsolvated diarsine complex[6] and differing from the DPM complex,[7] as expected on the basis of covalent radius differences between As and P. The Rh–As distances in the present structure (average 2.415 (1) Å) agree particularly well with those in the unsolvated DAM analogue (average 2.407 (1) Å) as do all As–C distances and Rh–As–C and As–C–As angles (Tables IV, V, and VII). As in both previous DAM and DPM determinations the methylene groups in the present structure are folded in a trans configuration with the carbon atom displaced 0.75 (1) Å from the Rh–As(1)–As(2) plane. Likewise the parameters involving the chloro and carbonyl ligands are as expected for a square-planar rhodium(I) complex and are especially close to the analogous distances in the unsolvated DAM and DPM species.

The unexpected features of this molecule all relate to the metal–metal separation (3.236 (2) Å), which, although in the range expected for nonbonded rhodium atoms, is significantly shorter than that observed for the unsolvated DAM analogue (3.396 (1) Å). The present distance is rather unusual in that it is shorter than the nonbonded As–As separation of 3.272 (2) Å. In bridging DPM and DAM complexes involving no formal metal–metal bond the opposite is generally true.[1–3,6,7,17–19] Therefore in the unsolvated DAM analogue the Rh–Rh separation is ca. 0.11 Å longer than the As–As separation. The shortening of the Rh–Rh distance in the present compound probably results from interactions with the CH_2Cl_2 of solvation, which as previously mentioned is directly along the Rh–Rh vector and can therefore result in a compression of this vector in the lattice. However the contacts giving rise to the compression do not seem to be simply between the CH_2Cl_2 molecule and the rhodium atoms, as one might expect; the shortest such contact is 4.600 (1) Å. Even the contacts between the CH_2Cl_2 molecule and the chloro and carbonyl ligands are not unusually short (see Table IV). Instead the reasons for the Rh–Rh shortening seem to be more subtle and may originate through the DAM framework. The orientations of the phenyl groups are intimately related to the orientations of the chloro and carbonyl ligands which are in turn related to the metal–metal separation (vide infra). We suggest therefore that the solvent molecule affects the Rh–Rh separation indirectly by influencing the phenyl ring orientations. On the basis of these orientations the metals assume a separation which then allows a minimization of nonbonded contacts.

Surprisingly the Rh–Rh separation is almost exactly that observed in the DPM analogue,[7] indicating that although the bite size of DAM is larger, on the whole, than that of DPM, considerable flexibility is allowed. This flexibility is seen in the tremendous range in M–M distances allowed in DPM- and DAM-bridged complexes, ranging from 2.46 to 3.38 Å for DPM and 2.52 to 3.81 Å for DAM.[20]

Other differences between the present determination and that of the unsolvated analogue, like the Rh–Rh compression, also result from the complex–solvate interactions in the present structure. Therefore in the present solvated species the rhodium square planes are much closer to planarity, because of the Rh–Rh compression, than in the unsolvated analogue (compare for example plane 2 in Table VI to the analogous plane in ref 6). Also, as noted earlier, the tilt of these square planes to the Rh–Rh vector is less in the present determination owing to nonbonded contacts between the phenyl groups and the chloro and carbonyl ligands in the somewhat more crowded environment as the metals approach each other (see Table IV). The twist of the rhodium planes occurs in order to minimize nonbonded contacts between the carbonyl and chloro ligands and the phenyl groups by staggering these groups. However, owing to the differing phenyl ring orientations with respect to the unsolvated species and the closer Rh–Rh separation, it seems that close contacts (both intra- and intermolecular) between the carbonyl and chloro ligands and the phenyl groups prevent any further twisting of the rhodium planes (see Figure 1).

The present structure is therefore useful in that, taken together with the structure determinations of the unsolvated DAM[6] and DPM[7] analogues, it gives us a valuable insight into the flexibility of these diarsine and diphosphine ligands. This flexibility is evident in the differences in Rh–Rh separations (0.160 (2) Å) in the solvated and unsolvated species. It seems that this significant change is brought about by packing considerations with the CH_2Cl_2 of crystallization resulting indirectly in compression along the Rh–Rh axis in the present structure. Also worthy of note is that the Rh–Rh separation is less than the intraligand As–As separation. A comparison of these relative distances has been used (often by us) as an indication of the existence of metal–metal interactions; if the metal–metal separation were less than the intraligand As–As or P–P separation (for DAM or DPM, respectively), this would be taken as an indication of a direct metal–metal interaction. However, in the present determination where the Rh–Rh distance is less than the As–As distance this seems not to result from any differences in metal–metal interaction between it and the unsolvated analogue but seems to result from packing. In fact, that the Rh–Rh separation is so readily modified by packing considerations is evidence that no direct metal–metal interaction is involved.

Although the presence of bridging DPM and DAM ligands seems to be an important factor in stabilizing the unusual ketonic carbonyl complexes,[1–3] observed differences in the stabilities of the DPM and DAM complexes are not readily explained solely on basis of steric arguments. Both ligands seem to be capable of regulating the metal–metal separation to that required in the ketonic carbonyl complexes, and the preference of these two ligands for this metal–metal separation we believe, on the basis of a comparison of this structure with those of the unsolvated DAM and DPM analogues, is slight.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada and The University of Alberta for financial support and The University of Alberta for a scholarship to S.K.D.

Registry No. *trans*-[RhCl(CO)(DAM)]$_2$·CH_2Cl_2, 76529-81-2.

Supplementary Material Available: Table VIII showing idealized hydrogen parameters and a listing of the observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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[17] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.

[18] Benner, L. S.; Olmstead, M. M.; Hope, H.; Balch, A. L. *J. Organomet. Chem.* **1978**, *153*, C31.

[19] Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

[20] Olmstead, M. M.; Lindsay, C. H.; Benner, L. S.; Balch, A. L. *J. Organomet. Chem.* **1979**, *179*, 289 and references therein.