duction of a second methyl group.

Additional support for the hydrogen bonding solvation effects comes from trends in the relative nucleophilicities of halide ions in protic and polar aprotic solvents. In methanol, the order of nucleophilicities is $I^- > Br^- > C^-$, but in dimethylformamide the order is reversed.[41] This is due to hydrogen bonding, which is important for small anions. Similarly, the rate of reaction of N_3^- with MeI increases by $\sim 10^4$ on going from methanol to DMF, where N_3^- is not as effectively solvated.[41]

The lower formation constant for 2-methoxypyridine with $MeHgOCOCF_3$ (compared to picoline) could in part be due to secondary interactions of the more ionic mercurial with the $-OCH_3$ group. An inductive effect in the σ framework due to the electronegative oxygen is most likely responsible for its diminished basicity. 2,2′-Bipyridyl was also examined to evaluate the equilibrium constant in what could potentially be a two coordinated MeHg(II) species. 2,2′-Bipyridyl has a small K_f (with MeHgOAc) in methylene chloride solvent. The attempted measurement in methanol was unsuccessful due to extensive line broadening of the mercury signal.

Conclusions

The data presented demonstrate the importance of hydrogen bonding and steric effects on complexation equilibria. The steric inhibition to hydrogen bonding in methanol solvent causes a reversal of the expected trend in the formation constants. Further, we feel that the coupling constants measured by Canty in CD_3OD (Table II), which show an increased complexation with increased substitution, can best be understood on the basis of the above explanation of an encumbrance to solvation. These data further suggest that complexation of heavy metals with bioorganic substrates in aqueous media may exhibit similar behavior and the metal may bind preferentially with a more hindered site.

Acknowledgment. We acknowledge support from the National Institutes of Health and the National Science Foundation. We also wish to thank Professor D. B. Rorabacher for helpful discussions concerning the measurements of equilibrium constants.

Registry No. MeHgI, 143-36-2; $MeHgOCOCF_3$, 21502-74-9; $MeHgNO_3$, 2374-27-8; MeHgOAc, 108-07-6; MeHg(py), 94750-89-7; MeHg(B)OAc (B = 2-methylpyridine), 94750-90-0; MeHg(B)OAc (B = 2,6-dimethylpyridine), 94750-91-1; MeHg(B)OAc (B = 2,6-di-*tert*-butylpyridine), 94750-93-3; MeHg(B)OAc (B = 2-methoxypyridine), 94750-95-5; MeHg(B)OAc (B = 2-ethylpyridine), 94750-96-6; MeHg(B)OAc (B = 2,6-dimethoxypyridine), 94750-98-8; MeHg(B)OAc (B = 2,2′-bipyridyl), 94750-99-9; $MeHg(py)OCOCF_3$, 94751-00-5; $[MeHg(B)OCOCF_3]_2$ (B = picoline), 94780-99-1; $MeHg(B)OCOCF_3$ (B = 2,6-dimethylpyridine), 94751-01-6; $MeHg(B)OCOCF_3$ (B = 2,6-di-*tert*-butylpyridine), 94751-02-7; $MeHg(B)OCOCF_3$ (B = 2-methoxypyridine), 94751-03-8; py, 110-86-1; 2-methylpyridine, 109-06-8; 2,6-dimethylpyridine, 108-48-5; 2,6-di-*tert*-butylpyridine, 585-48-8; 2-methoxypyridine, 1628-89-3; 2-ethylpyridine, 100-71-0; 2,6-dimethoxypyridine, 6231-18-1; 2,2′-bipyridine, 366-18-7; benzene, 71-43-2; silver acetate, 563-63-3; $MeHg(B)OCOCF_3$ (B = picoline), 94751-04-9.

Supplementary Material Available: Tables containing complete listing of interatomic distances and angles, anisotropic thermal parameters, equations of planes, hydrogen atom positional parameters, observed and calculated structure factors and a packing diagram (17 pages). Ordering information is given on any current masthead page.

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Structure of $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(Ph_2PCH_2PPh_2)_2][ClO_4]\cdot 0.866CH_2Cl_2$: An "A-Frame" Compound Containing a σ,π-Acetylido Group

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The structure of $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]$ has been determined. It is found to have an "A-frame" geometry in which the acetylide moiety is σ-bound to one metal and π-bound to the other. Owing to steric interactions between the *tert*-butyl group and the DPM phenyl groups the acetylide moiety is involved in only a weak π interaction with the second metal. This compound crystallizes with 0.866 (7) equiv of CH_2Cl_2 in the space group $P\bar{1}$ (a = 13.011 (4) Å, b = 20.765 (5) Å, c = 12.559 (2) Å, α = 90.73 (2)°, β = 117.45 (2)°, γ = 71.89 (2)°, and Z = 2). The structure was refined to R = 0.052 and R_w = 0.072 based on 332 parameters varied and 6596 unique observed reflections.

Introduction

The acetylide group ($:C{\equiv}CR^-$) is quasi-isoelectronic with the ubiquitous carbonyl ligand and consequently is found to parallel the latter somewhat in its binding modes. In polynuclear complexes, for example, the ligand can adopt the terminal binding mode[1] or it can bridge two or more metals in several ways.[1-8] Even in the simplest polynuclear case, in which the acetylide ligand is involved with only two metals, two bridging modes are observed; either it can

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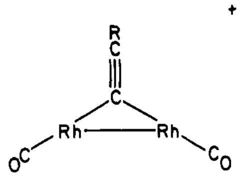
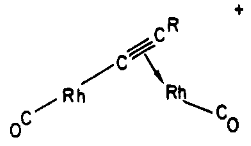
bind in an unsymmetrical manner,[1,5-8] σ-bound to one metal and π-bound to the other, or it can bind symmetrically,[2,3] much as is observed in "normal" bridging carbonyls (both modes are diagrammed below). In the former case the :C≡CR⁻ group functions as a four-electron donor to the two metals, whereas it is only a two-electron donor in the latter mode.

One such series of compounds which were of particular interest to us were the "A-frames" $[Rh_2(CO)_2(\mu\text{-}C_2R)(DPM)_2]^+$ (DPM = $Ph_2PCH_2PPh_2$). These species were prepared by Grundy and co-workers[9] and were found to be symmetrical on the NMR time scale over a range of temperatures between −80 and 25 °C, suggesting either that the acetylide groups were coordinated symmetrically or that they were unsymmetically bound and fluxional. For these compounds the two possible acetylide binding modes also give rise to differences in the nature of the metal–metal bonding. If the acetylide group is a symmetrically bonded two-electron donor, a Rh–Rh bond will be present (I) whereas if it is bonded in a σ,π manner (II), as a four-electron donor, there will be no Rh–Rh bond. Which of the two structures was actually present was of interest to us owing to the possibility of Rh–Rh bond reactivity in I.



I



II

Furthermore, a significant range in the acetylide C≡C stretches was observed in these compounds,[9] with R = H (i.e., :C≡CH⁻) this stretch appeared at 1887 cm⁻¹ whereas with R = Ph and *t*-Bu they appeared at 2021 and 2022 cm⁻¹, respectively. The structure of the *tert*-butylacetylide complex (as the perchlorate salt) was therefore undertaken in order to establish the acetylide ligand binding mode and to assist in explaining the differences in the IR spectra of the different acetylide-bridged complexes.

X-ray Data Collection

Well-formed orange single crystals of $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]\cdot 0.866CH_2Cl_2$ were kindly supplied by Dr. S. P. Deraniyagala and Prof. K. R. Grundy of Dalhousie University. One of these was mounted in air on a glass fiber. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 22 reflections, in the range 14.80° < 2θ < 28.32°, which were accurately centered on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The lack of systematic absences and the $\bar{1}$ diffraction symmetry suggested that the space group was either *P*1 or $P\bar{1}$. A cell reduction failed to show the presence of a higher symmetry cell.[10]

Intensity data were collected on a CAD4 diffractometer in the bisecting mode employing the ω–2θ scan technique up to 2θ = 48.0° with graphite-monochromated Mo Kα radiation. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure to assess possible crystal decomposition or movement. No significant variation in these standards was noted, so no correction was applied to the data. A total of 9133 reflections were collected and processed in the usual way by using a value of 0.04 for *p*.[11] Of these 6596 were unique and observed; only these were used in subsequent calculations. An absorption correction was applied to the data by using Gaussian integration.[12] See Table I for pertinent crystal data and the details of data collection.

Table I. Crystal Data and Intensity Collection Details for $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]\cdot 0.866CH_2Cl_2$

formula	$C_{58.866}H_{54.732}O_6P_4Cl_{2.732}Rh_2$
fw	1284.78
cell parameters	
a, Å	13.011 (4)
b, Å	20.765 (5)
c, Å	12.559 (2)
α, deg	90.73 (2)
β, deg	117.45 (2)
γ, deg	71.89 (2)
V, Å³	2827.4
Z	2
space group	$P\bar{1}$ (C_i^1)
d(calcd), g/cm³	1.509
temp, °C	23
radiatn λ, Å	graphite-monochromated Mo Kα (0.710 69)
receiving aperture, mm	2.00 + (0.500 tan θ) wide × 4.0 high, 173 from crystal
takeoff angle, deg	3.05
scan speed, deg/min	variable between 2.417 and 10.058
scan width, deg	0.65 + (0.350 tan θ) in ω
2θ limits, deg	0.10 ≤ 2θ ≤ 48.00
no. of unique collcd	9133
no. of unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	6596
cryst dimens, mm	0.21 × 0.18 × 0.47
abs coeff, cm⁻¹	8.637
range in transmissn coeff	0.829–0.866
no. of variables	332
error in observn of unit weight	2.20
R	0.052
R_w	0.072

Structure Solution and Refinement

The structure was solved in the space group $P\bar{1}$ by using standard Patterson and Fourier techniques. The alternate space group *P*1 was ruled out on the basis that refinement proceeded well in $P\bar{1}$ yielding acceptable position and thermal parameters and reasonable agreement indices. Furthermore, the location of all hydrogen atoms also argues in favor of the space group choice. Atomic scattering factors for the hydrogen[13] and non-hydrogen[14] atoms were taken from the usual sources and anomalous dispersion terms[15] for Rh, Cl, and P were included in F_c. The carbon atoms of the DPM phenyl groups were refined as rigid groups having idealized D_{6h} symmetry, C–C distances of 1.392 Å, and independent isotropic thermal parameters. All hydrogen atoms were input as fixed contributions; their idealized positions were recalculated after each cycle of refinement from the geometries of their attached carbon atoms by using C–H distances of 0.95 Å. These hydrogen atoms were assigned isotropic thermal parameters of 1 Å² greater than the *B* (or equivalent isotropic *B*) of their attached carbon atom.

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

Table II. Atomic Positional and Thermal Parameters[a]

atom	x	y	z	B_{eq},[b] Å^2
Rh(1)	0.19052 (4)	0.14265 (2)	0.00146 (4)	2.22
Rh(2)	0.09220 (4)	0.30326 (2)	−0.01138 (4)	2.48
Cl(1)[c]	−0.2431 (3)	0.2197 (1)	0.3614 (2)	7.83
Cl(2)	0.4957 (5)	0.4789 (2)	0.2399 (5)	13.76
Cl(3)	0.4250 (6)	0.4419 (3)	0.4036 (5)	15.25
P(1)	0.2266 (1)	0.1617 (1)	−0.1565 (1)	2.27
P(2)	0.1223 (1)	0.3187 (1)	−0.1751 (1)	2.41
P(3)	0.1572 (1)	0.1307 (1)	0.1645 (1)	2.51
P(4)	0.0606 (1)	0.2877 (1)	0.1511 (1)	2.55
O(1)	0.4087 (5)	0.0139 (3)	0.1049 (5)	5.34
O(2)	0.1695 (6)	0.4209 (3)	0.0817 (5)	6.44
O(3)	−0.2035 (8)	0.1933 (5)	0.2803 (7)	11.00
O(4)	−0.2266 (8)	0.1683 (4)	0.4433 (8)	9.91
O(5)	−0.3555 (10)	0.2629 (7)	0.3062 (9)	18.53
O(6)	−0.1632 (12)	0.2582 (5)	0.4352 (8)	15.94
C(1)	0.3292 (6)	0.0643 (3)	0.0686 (6)	3.23
C(2)	0.1428 (7)	0.3740 (4)	0.0476 (6)	4.02
C(3)	0.0230 (5)	0.2193 (3)	−0.0857 (5)	2.39
C(4)	−0.0814 (6)	0.2545 (3)	−0.1457 (6)	3.02
C(5)	−0.2160 (6)	0.2907 (4)	−0.2247 (6)	4.04
C(6)	−0.2576 (9)	0.2589 (10)	−0.3358 (10)	15.71
C(7)	−0.2824 (8)	0.2833 (8)	−0.1572 (11)	10.87
C(8)	−0.2447 (8)	0.3656 (6)	−0.2532 (17)	16.50
C(9)	0.1292 (5)	0.2442 (3)	−0.2535 (5)	2.40
C(10)	0.0425 (5)	0.2059 (3)	0.1713 (5)	2.79
C(S1)	0.5191 (22)	0.4235 (9)	0.3476 (22)	19.35

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] Equivalent isotropic B's. See supplementary material for anisotropic thermal parameters. [c] The numbering scheme for the perchlorate anion and the methylene chloride molecule is as follows: Cl(1), O(3), O(4), O(5), O(6) and C(S1), Cl(2), Cl(3), respectively.

The occupancy factors of the carbon and chlorine atoms of the methylene chloride molecule of solvation were initially refined individually and all three values converged to ca. 0.85, showing that the molecule was relatively well-behaved. In the final few cycles only one occupancy factor was varied for this solvent molecule and this converged to 0.866 (7). The thermal parameters on the methyl carbon atoms of the *tert*-butyl group and on the atoms of the solvent molecule were rather large so the atoms involved were removed from the least-squares refinements. However, they reappeared on a subsequent Fourier map in their original positions with no obvious signs of disorder so were reinserted and refined as previously.

The final model with 332 parameters varied converged to $R = 0.052$ and $R_w = 0.072$.[15] On the final difference Fourier map the highest 20 residuals (0.60–1.11 e Å^{-3}) were in the vicinities of the solvent molecule, the Rh atoms, and the methyl groups of the *tert*-butylacetylide group. A typical carbon atom on earlier syntheses had a peak intensity of about 7.0 e Å^{-3}. Without doubt, the refinement is hindered somewhat by the disordered ClO_4^- anion and CH_2Cl_2 solvent molecule and by the higher thermal motion of the *tert*-butyl group. However, the rest of the molecule is very well behaved with normal thermal parameters and very reasonable esd's on the associated bond lengths and angles.

The final positional and isotropic thermal parameters of the non-hydrogen atoms and the group parameters are given in Tables II and III, respectively. See the supplementary material for additional data.[17]

Description of Structure

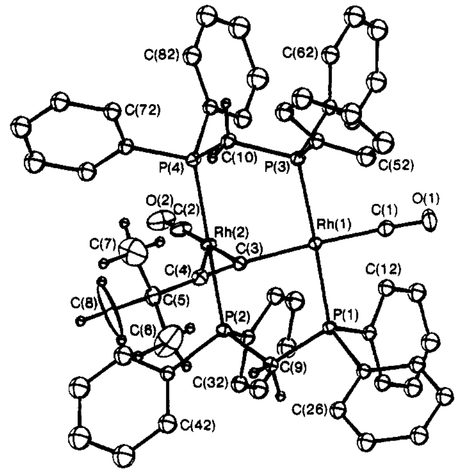

Figure 1. Perspective view of the complex cation $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2]^+$, showing the numbering scheme. The numbering of phenyl carbon starts at the atom bound to phosphorus; phenyl hydrogens have the same number as their attached carbon atom; 20% thermal ellipsoids are shown except for hydrogens which are drawn arbitrarily small.

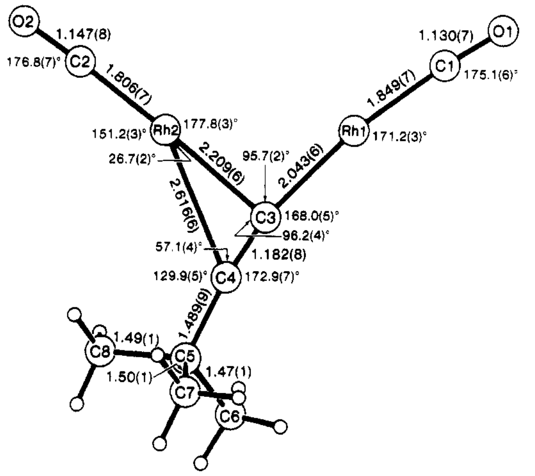

Figure 2. Representation of the inner coordination sphere in the plane through the Rh atoms and the acetylide ligand. Atoms are given arbitrary sizes.

A perspective view of the complex cation, showing the numbering scheme, is shown in Figure 1, and a representation of the inner coordination sphere in the plane of the rhodium atoms and the acetylide moiety is shown, with some relevant parameters, in Figure 2. More complete listings of interatomic distances and angles may be found in Tables IV and V, respectively.

The unit cell contains two $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2]^+$ cations, two perchlorate anions, and 1.732 molecules of methylene chloride. There are no unusual contacts between the ions or solvent molecules in the cell. Both the perchlorate anion and the methylene chloride molecule have the expected tetrahedral or pseudotetrahedral geometries although the large thermal parameters of the atoms suggest some degree of disorder. In spite of this presumed disorder, the Cl–O distances (range 1.300 (9)–1.480 (9) Å) and the O–Cl–O angles (range 105.6 (5)–112.7 (7)°) in the ClO_4^- anion are comparable to those in other determinations.[18] Similarly, the C–Cl distances (average 1.63 (2) Å) and the Cl(2)–C(S1)–Cl(3) angle (118.8 (3)°) in the CH_2Cl_2 molecule are normal.

The geometry of the complex cation is that of a rather undistorted "A-frame" and quite closely resembles two

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(17) Supplementary material.

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Table III. Parameters for the Rigid Groups

(a) Derived Parameters

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.3825 (3)	0.1576 (2)	−0.1152 (3)	2.6 (1)	C(51)	0.0979 (4)	0.0622 (2)	0.1694 (4)	2.9 (1)
C(12)	0.4708 (4)	0.1481 (2)	0.0063 (3)	3.4 (1)	C(52)	0.1547 (4)	−0.0017 (2)	0.1483 (4)	4.8 (2)
C(13)	0.5900 (3)	0.1445 (3)	0.0368 (3)	4.3 (1)	C(53)	0.1169 (5)	−0.0565 (2)	0.1554 (5)	6.0 (2)
C(14)	0.6209 (3)	0.1503 (3)	−0.0541 (4)	4.7 (2)	C(54)	0.0223 (5)	−0.0475 (2)	0.1838 (5)	5.5 (2)
C(15)	0.5326 (4)	0.1598 (2)	−0.1756 (3)	4.5 (2)	C(55)	−0.0346 (4)	0.0163 (3)	0.2049 (5)	5.5 (2)
C(16)	0.4134 (3)	0.1634 (2)	−0.2061 (3)	3.3 (1)	C(56)	0.0032 (4)	0.0712 (2)	0.1977 (4)	4.2 (1)
C(21)	0.2004 (4)	0.1008 (2)	−0.2640 (3)	2.7 (1)	C(61)	0.2932 (3)	0.1132 (2)	0.3131 (3)	2.9 (1)
C(22)	0.2908 (3)	0.0361 (2)	−0.2287 (3)	3.3 (1)	C(62)	0.2914 (4)	0.0915 (3)	0.4164 (4)	4.1 (1)
C(23)	0.2763 (4)	−0.0125 (2)	−0.3068 (4)	4.0 (1)	C(63)	0.3958 (5)	0.0778 (3)	0.5297 (3)	5.6 (2)
C(24)	0.1714 (4)	0.0036 (2)	−0.4201 (3)	4.2 (1)	C(64)	0.5020 (4)	0.0857 (3)	0.5396 (3)	5.5 (2)
C(25)	0.0810 (3)	0.0683 (2)	−0.4553 (3)	4.3 (1)	C(65)	0.5039 (3)	0.1074 (3)	0.4363 (4)	5.3 (2)
C(26)	0.0956 (3)	0.1169 (2)	−0.3773 (4)	3.5 (1)	C(66)	0.3995 (4)	0.1212 (2)	0.3231 (3)	4.0 (1)
C(31)	0.2611 (3)	0.3373 (2)	−0.1396 (3)	2.6 (1)	C(71)	−0.0803 (3)	0.3493 (2)	0.1387 (4)	3.0 (1)
C(32)	0.2683 (3)	0.3729 (2)	−0.2277 (3)	3.4 (1)	C(72)	−0.1490 (4)	0.3319 (2)	0.1843 (4)	3.8 (1)
C(33)	0.3762 (4)	0.3856 (2)	−0.1997 (4)	4.6 (2)	C(73)	−0.2545 (4)	0.3814 (2)	0.1754 (4)	4.5 (1)
C(34)	0.4770 (3)	0.3626 (3)	−0.0838 (4)	4.9 (2)	C(74)	−0.2914 (4)	0.4483 (2)	0.1208 (5)	5.5 (2)
C(35)	0.4699 (3)	0.3270 (2)	−0.0043 (3)	4.6 (2)	C(75)	−0.2227 (5)	0.4657 (2)	0.0751 (5)	5.6 (2)
C(36)	0.3619 (4)	0.3143 (2)	−0.0237 (3)	3.7 (1)	C(76)	−0.1172 (4)	0.4162 (2)	0.0841 (4)	4.3 (1)
C(41)	0.0035 (4)	0.3890 (2)	−0.2943 (3)	2.6 (1)	C(81)	0.1809 (3)	0.2908 (2)	0.2997 (3)	2.9 (1)
C(42)	−0.0504 (5)	0.3826 (2)	−0.4169 (4)	4.4 (2)	C(82)	0.1593 (4)	0.2971 (3)	0.3986 (4)	4.3 (1)
C(43)	−0.1357 (5)	0.4400 (3)	−0.5039 (3)	6.3 (2)	C(83)	0.2534 (5)	0.2971 (3)	0.5128 (3)	5.6 (2)
C(44)	−0.1670 (5)	0.5038 (2)	−0.4683 (4)	6.5 (2)	C(84)	0.3693 (4)	0.2907 (3)	0.5280 (3)	6.0 (2)
C(45)	−0.1130 (5)	0.5102 (2)	−0.3458 (5)	5.8 (2)	C(85)	0.3910 (3)	0.2843 (3)	0.4291 (5)	5.9 (2)
C(46)	−0.0278 (4)	0.4528 (2)	−0.2588 (3)	4.6 (2)	C(86)	0.2968 (4)	0.2843 (2)	0.3149 (4)	4.1 (1)

(b) Rigid-Group Parameters

	x_c[a]	y_c	z_c	ϕ[b]	θ	ρ
group 1	0.5017 (3)	0.1540 (1)	−0.0847 (3)	1.382 (10)	1.837 (2)	−1.095 (10)
group 2	0.1859 (3)	0.0522 (1)	−0.3420 (2)	1.164 (3)	2.845 (2)	−2.406 (3)
group 3	0.3691 (3)	0.3500 (1)	−0.1117 (3)	−2.279 (4)	−2.159 (3)	−2.755 (4)
group 4	−0.0817 (3)	0.4464 (2)	−0.3813 (3)	−0.160 (5)	−2.266 (3)	−2.425 (5)
group 5	0.0601 (3)	0.0073 (2)	0.1766 (3)	1.073 (3)	2.289 (3)	2.846 (4)
group 6	0.3976 (3)	0.0995 (2)	0.4264 (3)	−0.832 (4)	2.289 (3)	1.065 (4)
group 7	−0.1858 (3)	0.3988 (2)	0.1297 (3)	−0.180 (3)	2.497 (3)	2.660 (3)
group 8	0.2751 (3)	0.2907 (2)	0.4139 (3)	−1.370 (5)	2.254 (3)	1.680 (5)

[a] x_c, y_c, and z_c are the fractional coordinates of the centroid of the rigid group. [b] The rigid-group orientation angles have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.

Table IV. Relevant Distances (Å) in $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]\cdot 0.866CH_2Cl_2$

(a) Bonded Contacts

Rh(1)-P(1)	2.303 (2)	P(1)-C(11)	1.821 (4)
Rh(1)-P(3)	2.311 (2)	P(1)-C(21)	1.828 (4)
Rh(1)-C(1)	1.849 (7)	P(2)-C(9)	1.824 (6)
Rh(1)-C(3)	2.043 (6)	P(2)-C(31)	1.815 (5)
Rh(2)-P(2)	2.307 (2)	P(2)-C(41)	1.811 (3)
Rh(2)-P(4)	2.305 (2)	P(3)-C(10)	1.827 (6)
Rh(2)-C(2)	1.806 (7)	P(3)-C(51)	1.832 (6)
Rh(2)-C(3)	2.209 (6)	P(3)-C(61)	1.822 (3)
Rh(2)-C(4)	2.616 (6)	P(4)-C(10)	1.823 (6)
C(1)-O(1)	1.130 (7)	P(4)-C(71)	1.817 (5)
C(2)-O(2)	1.147 (8)	P(4)-C(81)	1.817 (4)
C(3)-C(4)	1.182 (8)	Cl(1)-O(3)[a]	1.376 (7)
C(4)-C(5)	1.489 (9)	Cl(1)-O(4)[a]	1.387 (7)
C(5)-C(6)	1.47 (1)	Cl(1)-O(5)[a]	1.300 (9)
C(5)-C(7)	1.50 (1)	Cl(1)-O(6)[a]	1.480 (9)
C(5)-C(8)	1.49 (1)	C(S1)-Cl(2)[b]	1.64 (2)
P(1)-C(9)	1.818 (6)	C(S1)-Cl(3)[b]	1.62 (2)

(b) Nonbonded Contacts

Rh(1)-Rh(2)	3.155 (1)	H1(C7)-C(71)	3.06
P(1)-P(2)	3.082 (2)	H2(C8)-C(41)	2.83
P(3)-P(4)	3.084 (2)	H2(C8)-C(42)	3.06

[a] ClO_4^- anion. [b] CH_2Cl_2 solvent molecule.

other structurally characterized rhodium A-frames, $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$[19] and $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$.[20] Within the $Rh_2(DPM)_2$ framework the geometry is normal for such a species, having all Rh–P distances in good agreement with each other and with previous reports on DPM-bridged binuclear rhodium complexes.[19-22] The orientations of the DPM ligands are such as to minimize nonbonded contacts between the phenyl groups and the equatorial ligands. For this reason the both methylene groups are bent toward the bridging acetylide group thrusting four phenyl groups into the otherwise vacant positions on the opposite face of the compound. The Rh–Rh distance of 3.155 (1) Å matches almost exactly those of the related sulfide-bridged (3.154 (2) Å) and chloride-bridged (3.1520 (8) Å) "A-frames", suggesting that no Rh–Rh bond is present. This is consistent with the intraligand P–P distances (average 3.083 (2) Å) which are less than the metal–metal separation, indicating that there is no significant mutual attraction of the metals.

The carbonyl geometries are quite unspectacular and are normal for such terminally bound groups.

As diagrammed in Figures 1 and 2, the acetylide group is bridging in the more commonly observed σ,π mode,[5-8] in which C(3) is σ-bound to Rh(1) and the unsaturated acetylenic bond (C(3)–C(4)) is side-on coordinated to Rh(2). In this coordination mode the acetylide group behaves electronically very much like the bridging sulfide and chloride ligands in the previously mentioned "A-frames", functioning as a two-electron donor to each metal.

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Table V. Selected Angles (deg) in $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]\cdot 0.866CH_2Cl_2$

P(1)-Rh(1)-P(3)	175.81 (6)	C(6)-C(5)-C(8)	111.8 (12)	C(9)-P(2)-C(41)	103.8 (2)
C(1)-Rh(1)-C(3)	171.2 (3)	C(7)-C(5)-C(8)	106.5 (10)	C(31)-P(2)-C(41)	102.3 (2)
P(2)-Rh(2)-P(4)	179.53 (6)	Rh(1)-P(1)-C(9)	114.7 (2)	C(10)-P(3)-C(51)	102.2 (3)
C(2)-Rh(2)-C(3)	177.8 (3)	Rh(1)-P(1)-C(11)	116.4 (1)	C(10)-P(3)-C(61)	104.7 (2)
C(2)-Rh(2)-C(4)	151.2 (3)	Rh(1)-P(1)-C(21)	114.5 (2)	C(51)-P(3)-C(61)	103.5 (2)
C(3)-Rh(2)-C(4)	26.7 (2)	Rh(1)-P(3)-C(10)	114.1 (2)	C(10)-P(4)-C(71)	102.5 (3)
Rh(1)-C(1)-O(1)	175.1 (6)	Rh(1)-P(3)-C(51)	115.8 (2)	C(10)-P(4)-C(81)	103.5 (2)
Rh(2)-C(2)-O(2)	176.8 (7)	Rh(1)-P(3)-C(61)	114.9 (2)	C(71)-P(4)-C(81)	104.7 (2)
Rh(1)-C(3)-Rh(2)	95.7 (2)	Rh(2)-P(2)-C(9)	112.5 (2)	P(1)-C(9)-P(2)	115.6 (3)
Rh(1)-C(3)-C(4)	168.0 (5)	Rh(2)-P(2)-C(31)	115.2 (1)	P(3)-C(10)-P(4)	115.3 (3)
Rh(2)-C(3)-C(4)	96.2 (4)	Rh(2)-P(2)-C(41)	115.7 (2)	O(3)-Cl(1)-O(4)	111.9 (6)
Rh(2)-C(4)-C(3)	57.1 (4)	Rh(2)-P(4)-C(10)	114.1 (2)	O(3)-Cl(1)-O(5)	111.7 (6)
Rh(2)-C(4)-C(5)	129.9 (5)	Rh(2)-P(4)-C(71)	114.0 (2)	O(3)-Cl(1)-O(6)	107.4 (7)
C(3)-C(4)-C(5)	172.9 (7)	Rh(2)-P(4)-C(81)	116.4 (2)	O(4)-Cl(1)-O(5)	112.7 (7)
C(4)-C(5)-C(6)	108.6 (6)	C(9)-P(1)-C(11)	104.1 (3)	O(4)-Cl(1)-O(6)	105.6 (5)
C(4)-C(5)-C(7)	108.7 (6)	C(9)-P(1)-C(21)	102.9 (2)	O(5)-Cl(1)-O(6)	107.1 (8)
C(4)-C(5)-C(8)	111.4 (6)	C(11)-P(1)-C(21)	102.5 (2)	Cl(2)-C(S1)-Cl(3)	118.8 (3)
C(6)-C(5)-C(7)	109.8 (10)	C(9)-P(2)-C(31)	106.1 (3)		

Overall the geometry of the bridging acetylide moiety is similar to those previously reported. Therefore the carbon atom which is bound to both metals (C(3)) is closer to the metal to which it is σ-bonded (2.043 (6) Å vs. 2.209 (6) Å) and both of these distances are in line with those in other reports.[1,5-8] The angles at C(3) clearly show the asymmetry of the acetylide binding, with Rh(1)–C(3)–C(4), at 168.0 (5)°, being much greater than Rh(2)–C(3)–C(4) (96.2 (4)°). This group, however, does show some appreciable differences from those in previous determinations.[1,5-8] Most notably, the outermost acetylido carbon atom (C(4)) is much farther from Rh(2) (2.616 (6) Å) than equivalent distances in other structures (2.00 (1)–2.47 (1) Å), and as a result the present π interaction with Rh(2) must be considered to be rather weak. This weak interaction results in smaller bend-back angles at C(3) and C(4) (168.0 (5) and 172.9 (7)°, respectively) than previously reported and also results in one of the shortest reported acetylide C≡C distances of 1.182 (8) Å; this value is actually less than that in uncoordinated acetylene.[23] The reason for the weak π interaction involving Rh(2) seems to be steric in origin; C(4) cannot get closer to Rh(2) owing to unfavorable nonbonded contacts between the bulky *tert*-butyl group and the DPM phenyl groups. The worst of these interactions, involving rings 4 and 7 (see Table IV and Figure 1), clearly are such as to prevent closer approach of the acetylide group to Rh(2). It is to be noted that the slight bending of the acetylide group is cis; trans bending has also been reported.[6,7,24]

The C(4)–C(5) distance is exactly that expected based on the covalent radii of the sp- and sp^3-hybridized carbon atoms, but the C(5)–methyl distances (average 1.49 (1) Å) are slightly shorter than expected (1.54 Å). This latter discrepancy is most probably a manifestation of the large thermal amplitudes associated with the methyl groups. All angles at C(5) are close to the tetrahedral value. The rather wide Rh(1)–C(3)–Rh(2) angle of 95.7 (2)° is again consistent with the absence of a Rh–Rh bond in the compound.

Discussion

In the Introduction of this paper, it was noted that the C≡C stretch for the coordinated acetylide group in the complex $[Rh_2(CO)_2(\mu\text{-}C_2H)(DPM)_2]^+$ was significantly lower than those of the phenyl- and *tert*-butyl substituted analogues (1887 cm^{-1} vs. 2021 and 2022 cm^{-1}, respectively).[9] By comparison, the C≡C stretches for σ,π-bound acetylides have been reported in the range from ca. 1800 to 2035 cm^{-1} [1,25] and the analogous stretches for a series of symmetrically bound acetylides have been reported near 2040 cm^{-1}.[26] One possible explanation for the very different C≡C stretches in the A-frame complexes is that the coordination modes of the acetylides differ. However, on the basis of the structure determination of $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2]^+$, this seems not to be the case; rather, we suggest that the above spectroscopic differences arise from the steric differences between the acetylide groups. We suggest that all three complexes have essentially the geometry observed for the *tert*-butylacetylide species, in which the acetylide moiety is σ-bound to one metal and π-bound to the second. In these complexes, the strength of the latter interaction seems to be limited by the bulk of the acetylide substituent. For the large *tert*-butyl substituent the interactions between it and the DPM phenyl groups limit effective interaction between the acetylenic bond and the second metal. As a result, the acetylide group is perturbed only slightly from a normal terminally bound group and therefore displays a high C≡C stretch.[1,27] The bulky phenylacetylide group presumably coordinates in a similar manner. However, with the unsubstituted acetylide group, steric interactions of the acetylide hydrogen and the DPM ligands will be minimal so this group should be capable of achieving a strong π interaction with the second metal. In agreement with this, the C≡C stretch is quite low, suggesting significant lowering of the acetylide bond order.

The nature of the acetylide bonding mode (i.e., symmetric bridging or σ,π bridging) was also of interest to us owing to the nature of the accompanying metal–metal interaction. Grundy and Deraniyagala had observed[9] that the above acetylide-bridged compounds reacted with CO to give the tricarbonyl species $[Rh_2(CO)_2(\mu\text{-}C_2R)(\mu\text{-}CO)(DPM)_2]^+$. If the dicarbonyl precursors had structure I, one possibility would be that CO insertion into the Rh–Rh bond could occur to give the symmetrically bridged species having no accompanying Rh–Rh bond. We thought this highly unlikely owing to the severe nonbonded contacts that would result between the bridging carbonyl and acetylide groups.[28] The structure determination of the

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tert-butylacetylide precursor of course indicates that structure II and not I is present, and therefore reaction with CO is readily interpreted as occurring in a manner exactly analogous to that in the chloro-bridged analogue; CO coordination is accompanied by the formation of a Rh–Rh bond. Although it is possible that CO coordination could be accomplished by a change in the acetylide bonding mode, we feel that this is unlikely in the present series of compounds. Not only would the above mentioned unfavorable contacts between the bridging CO and acetylide group result, but also the spectroscopic parameters[29] for the CO adducts agree very well with those of the analogous chloro-bridged species,[30] suggesting similar structure for these complexes.

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Registry No. $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]\cdot 0.866CH_2CL_2$, 95217-03-1; $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]$, 94294-51-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, the derived hydrogen positions, and the observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead page.

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(28) Without a metal–metal bond the carbon atoms of the bridging carbonyl and acetylide groups can be viewed as sp^2 hybridized and come into rather close contact. For a discussion of insertions into metal–metal bonds see: Cowie, M.; Dickson, R. S.; Hames, B. W. *Organometallics* **1984**, *3*, 1879.

(29) For the complexes $[Rh_2(CO)_2(\mu\text{-}C_2R)(\mu\text{-}CO)(DPM)_2]^+$ (R = H, Ph) the carbonyl stretches are at 1987, 1973, and 1856 cm^{-1} and at 1988, 1969, and 1872 cm^{-1}, respectively.

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Cleavage of C–S Bond in Allylic Aryl Sulfides Promoted by Rhodium Hydride Complex: Reaction Mechanisms of Allyl–Sulfur Bond Fission[†]

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Reactions of allylic aryl sulfides with $RhH(PPh_3)_4$ cause cleavage of allylic sulfur bond to afford rhodium thiolato complexes $[Rh(\mu\text{-}SAr)(PPh_3)_2]_2$ and olefins under mild conditions. Distributions of olefinic products in the reactions of sulfides having alkyl substituents on the allyl part such as 3-(phenylthio)-1-butene and 1-(phenylthio)-2-butene indicate that selective rearrangement of C=C bond occurs. The reaction of 3-(phenylthio)propene with $RhD(P(C_6D_5)_3)_4$ gives propylene as a mixture of C_3H_6, C_3H_5D, $C_3H_4D_2$, and $C_3H_3D_3$ with recovery of partly deuterated 3-(phenylthio)propene, suggesting hydrogen exchange between 3-(phenylthio)propene and rhodium hydride complex prior to the C–S bond cleavage. New rhodium thiolato complexes obtained from these reactions are characterized by IR and/or NMR spectroscopy, elemental analysis, and their chemical reactions.

Introduction

Recently, various synthetic methods utilizing allyl–halogen, allyl–oxygen, and allyl–sulfur bond cleavage have been developed and successfully employed in synthetic organic chemistry.[1] Palladium and nickel complex catalyzed cross-coupling reactions of allylic electrophiles with nucleophilic reagents also are of interest.[2-6] In most of these reactions π-allyl complex intermediates are believed to be formed by direct bond cleavage induced by zerovalent complexes. However, reactions of allylic electrophiles with transition-metal complexes have been studied mainly with nickel and palladium complexes. Previous studies of our group revealed that reaction features of allylic carboxylates and allylic carbonates with group 8–10 metal hydrides[7] differ distinctly from those involving direct cleavage of allyl–oxygen bond induced by zerovalent nickel and palladium complexes.[8]

We have communicated in a preliminary note[9] that cleavage of the allyl–sulfur bond in allylic aryl sulfides

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[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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