filtrate was treated with an excess of MeCN or CO. Removal of the volatiles and crystallization of the residual solid from dichloromethane/pentane afforded *trans*-[PtH(MeCN)(As(t-Bu)$_3$)$_2$]X or *trans*-[PtH(CO)(As(t-Bu)$_3$)$_2$]X, respectively, in 90% yield.

Reaction of *trans*-PtHCl(As(t-Bu)$_3$)$_2$ with P(t-Bu)$_3$. A solution of the phosphine (0.5 mmol) in pentane (5 mL) was added dropwise to the platinum complex (0.5 mmol) in pentane (15 mL). The reaction mixture was stirred for 2 h and then freed from the solvent. Infrared and ^{1}H NMR spectra of the residual colorless solid showed it to be a mixture of *trans*-PtHCl(As(t-Bu)$_3$)(P(t-Bu)$_3$), *trans*-PtHCl(P(t-Bu)$_3$)$_2$, and *trans*-PtHCl(As(t-Bu)$_3$)$_2$.

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Registry No. **1**, 80630-41-7; **2**, 80630-42-8; **3**, 80630-43-9; **4**, 80630-44-0; **5**, 80630-45-1; **6**, 80630-46-2; **7**, 80630-47-3; **8**, X = BF$_4$, 80630-49-5; **8**, X = PF$_6$, 80630-50-8; **8**, X = ClO$_4$, 80630-51-9; **9**, 80630-53-1; **10**, 80630-55-3; **11**, X = PF$_6$, 80630-57-5; **11**, X = ClO$_4$, 80630-58-6; **11**, X = BF$_4$, 80630-59-7; **12**, 80630-60-0; *trans*-PtHCl(P(t-Bu)$_3$)$_2$, 67901-08-0; K$_2$PtCl$_4$, 10025-99-7.

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Binuclear Cationic Complexes of Rhodium. 6. Carboxylate and Acetylene Derivatives[1]

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The A-frame complexes [Rh$_2$(CO)$_2$(μ-Cl)(L$_2$)$_2$]PF$_6$ (L$_2$ = (C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$ (DPM), (C$_6$H$_5$)$_2$AsCH$_2$As(C$_6$H$_5$)$_2$ (DAM)) react with silver carboxylates to yield the carboxylate-bridged dimers [Rh$_2$(CO)$_2$(μ-O$_2$CR)(L$_2$)$_2$]PF$_6$ (L$_2$ = DPM, R = CH$_3$; L$_2$ = DAM, R = CH$_3$, C$_2$H$_5$). All three complexes rapidly exchange carbon monoxide at room temperature, but only for the phosphine complex could a μ-carbonyl adduct be detected. Reaction of the carboxylate dimers with electronegatively substituted acetylenes yields the vinylidene-bridged species [Rh$_2$(CO)(μ-CO)(μ-RC$_2$R)(O$_2$CR′)(L$_2$)$_2$]PF$_6$ (L$_2$ = DPM, DAM, R = CO$_2$CH$_3$, CF$_3$, R′ = CH$_3$; L$_2$ = DAM, R = CO$_2$CH$_3$, CF$_3$, R′ = C$_2$H$_5$). These in turn react with other ligands L (L = CNC(CH$_3$)$_3$, P(OCH$_3$)$_3$) to yield [Rh$_2$(L)(μ-CO)(μ-RC$_2$R)(O$_2$CCH$_3$)(L$_2$)$_2$]PF$_6$. The complex [Rh$_2$(CNC(CH$_3$)$_3$)$_4$(DPM)$_2$](B(C$_6$H$_5$)$_4$)$_2$ also reacts with electronegatively substituted acetylenes to give [Rh$_2$(CNC(CH$_3$)$_3$)$_4$(RC$_2$R)(DPM)$_2$](B(C$_6$H$_5$)$_4$)$_2$. The infrared and ^{1}H, ^{13}C, and ^{31}P NMR spectra of these complexes are also discussed.

Introduction

In the course of our study of the face-to-face dimers [Rh(CO)ClL$_2$]$_2$ (L$_2$ = (C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$ (DPM), (C$_6$H$_5$)$_2$AsCH$_2$As(C$_6$H$_5$)$_2$ (DAM))[1] it was observed that they reacted readily with hexafluorobut-2-yne to yield an extremely insoluble olive green product.[2] More recently a very similar product was obtained in the reaction of this acetylene with the A-frame complexes [Rh$_2$(CO)$_2$(μ-Cl)(L$_2$)$_2$]B(C$_6$H$_5$)$_4$ (L$_2$ = DPM, DAM).[3] Because of our interest in the mode of interaction of carbon–carbon multiple bonds with binuclear complexes, we sought related acetylene adducts that would be sufficiently soluble to permit adequate characterization. We report here on the results of this study.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under an atmosphere of dinitrogen. Reactions were carried out in a dinitrogen atmosphere with use of standard Schlenk techniques. Literature procedures were used to prepare [Rh$_2$(CO)$_2$(μ-Cl)(L$_2$)$_2$]PF$_6$[1] and [Rh$_2$(CNC(CH$_3$)$_3$)$_4$(DPM)$_2$](B(C$_6$H$_5$)$_4$)$_2$[4]. Infrared spectra were obtained on Beckman IR-18A and Perkin-Elmer 298 spectrophotometers. Carbon-13 and phosphorus-31 NMR spectra were obtained on a JEOL FX-60 spectrometer operating at 15.03 MHz (30° flip angle, 5-s repetition rate) and 24.15 MHz (45° flip angle, 5-s repetition rate), respectively. Chemical shifts are referred to external tetramethylsilane (^{13}C) and external H$_3$PO$_4$ (^{31}P), respectively, and are positive downfield. Proton NMR spectra were obtained on JEOL MH-100 and Varian EM-390 spectrometers at 100 and 90 MHz, respectively, and are referenced to internal tetramethylsilane (τ 10.0). Simulation of NMR spectra was accomplished with use of a local version of the LAOCOON-3[14] program. Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Conductance measurements were made on a Thomas-Serfass Model RCM 15B1 bridge with a cell containing platinized electrodes, which had been calibrated with 0.01 M aqueous potassium chloride.

Synthesis of [Rh$_2$(CO)$_2$(μ-O$_2$CR)(L$_2$)$_2$]PF$_6$ (L$_2$ = DPM, DAM, R = CH$_3$; L$_2$ = DAM, R = C$_2$H$_5$). In a typical experiment, 0.300 mmol of the appropriate [Rh$_2$(CO)$_2$(μ-Cl)(L$_2$)$_2$]PF$_6$ complex was dissolved in 20 mL of a 1:1 (v/v) mixture of dichloromethane and tetrahydrofuran and treated with an equimolar quantity of solid silver carboxylate. The resulting suspension was stirred vigorously for 4 h while protected from light during which time the color changed from red orange to dark red. Following filtration through a pad of diatomaceous earth the solution was concentrated under reduced pressure until solid formed. The precipitation was completed by addition of diethyl ether, and the resulting product recrystallized from dichloromethane/diethyl ether to yield red-orange to dark red crystals, which were collected and dried in vacuo. All products appear to be air-stable.

Synthesis of Acetylene Adducts, [Rh$_2$(CO)(μ-CO)(μ-RC=CR)(O$_2$CR′)(L$_2$)$_2$]PF$_6$ (L$_2$ = DPM, DAM, R = CF$_3$, CO$_2$CH$_3$, R′ = CH$_3$; L$_2$ = DAM, R = CF$_3$, CO$_2$CH$_3$, R′ = C$_2$H$_5$). In a typical experiment, 0.200 mmol of [Rh$_2$(CO)$_2$(μ-O$_2$CR′)(L$_2$)$_2$]PF$_6$ was dissolved in 5 mL of dichloromethane and treated with an excess of the appropriate acetylene. After 2 h of stirring, the solution had become light orange, and addition of diethyl ether precipitated the product, which was collected and recrystallized from dichloromethane/diethyl ether to yield yellow air-stable microcrystals.

Synthesis of [Rh$_2$(L)(μ-CO)(μ-RC=CR)(O$_2$CCH$_3$)(L$_2$)$_2$]PF$_6$ (L = CNC(CH$_3$)$_3$, P(OCH$_3$)$_3$; R = CF$_3$, CO$_2$CH$_3$; L$_2$ = DPM, DAM). In a typical experiment, 0.200 mmol of [Rh$_2$(CO)$_2$(RC=CR)(O$_2$CCH$_3$)(L$_2$)$_2$]PF$_6$ was dissolved in 10 mL of dichloromethane and 1.5 equiv of the ligand (*tert*-butyl isocyanide or trimethyl phosphite) was added. For the reactions with the isocyanide the

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[1] Part 1: Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1969**, *8*, 119. Part 2: Mague, J. T. *Ibid.* **1969**, *8*, 1975. Part 3: Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628. Part 4: Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060. Part 5: Mague, J. T.; DeVries, S. H. *Ibid.* **1980**, *19*, 3743.

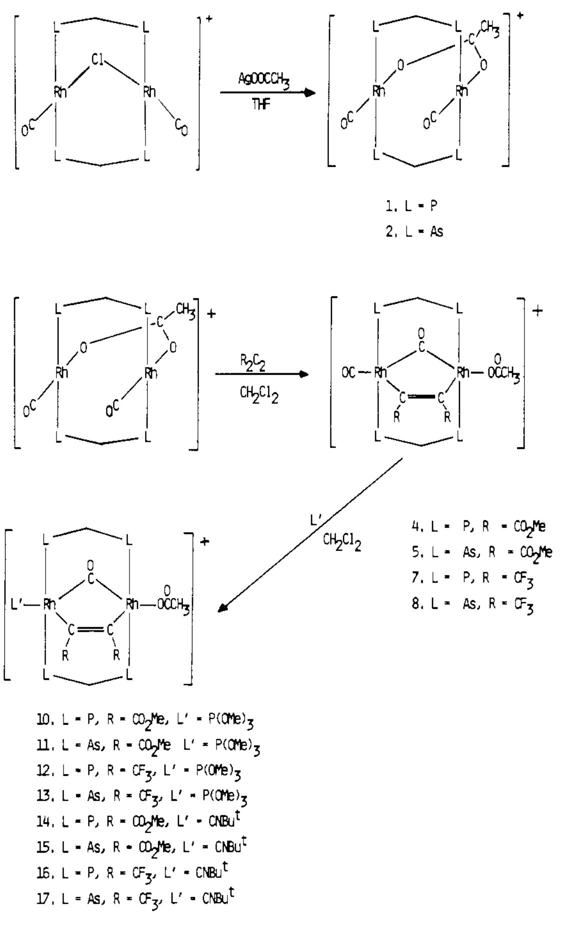
[2] Nutt, M. O. M.S. Thesis, Tulane University, 1969.

[3] Mague, J. T., unpublished results.

[4] Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049.

0020-1669/82/1321-1632$01.25/0

Scheme I



mixture was stirred overnight at room temperature while with trimethyl phosphite it was necessary to reflux the solution for the same period of time. Dilution of the resulting solution with diethyl ether afforded the products as orange air-stable crystals, which were recrystallized from dichloromethane/diethyl ether and dried in vacuo.

$[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}CH_3O_2CC_2CO_2CH_3)(DPM)_2](B(C_6H_5)_4)_2$. To a dichloromethane solution (10 mL) of 0.216 g (0.111 mmol) of $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$ was added 0.033 g (0.222 mmol) of dimethyl acetylenedicarboxylate. After overnight stirring at room temperature the original magenta solution had become orange. Dilution with diethyl ether precipitated a yellow powder, which was recrystallized from dichloromethne/diethyl ether to yield the product as dull yellow, air-stable microcrystals.

$[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}CF_3C_2CF_3)(DPM)_2](B(C_6H_5)_4)_2$. This was prepared in analogous fashion to the previous complex by stirring the solution in a serum-capped flask in an atmosphere of hexafluorobut-2-yne overnight. The product was obtained as pale brownish pink flakes by precipitation with diethyl ether and was recrystallized from dichloromethane/diethyl ether.

Results and Discussion

Analytical data for the new complexes are presented in Table I (supplementary material) while infrared and NMR spectral data are given in Tables II and III, respectively. Conductance data appear in Table IV (supplementary material). Scheme I depicts the chemistry of the acetate complexes. That of the propionate derivatives is strictly analogous.

The bridging chloride ligand in the A-frame complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]PF_6$ (L_2 = DPM, DAM) is labile and can be readily removed upon reaction with a variety of silver salts. When they are reacted with silver carboxylates, red to orange complexes analyzing as $[Rh_2(CO)_2(O_2CR)(L_2)_2]PF_6$ (L_2 = DPM, R = CH_3 (**1**); L_2 = DAM, R = CH_3 (**2**), C_2H_5 (**3**)) are obtained (Scheme I). The observance of 1:1 electrolyte behavior indicates coordination of the carboxylate group, and the appearance of a band of medium intensity in the 1520–1530-cm^{-1} region is consistent with the carboxylate

Table II. Infrared Spectroscopic Data[a]

complex	$\nu_{^{12}C\equiv O}$, cm^{-1}	$\nu_{^{13}C\equiv O}$, cm^{-1}	other freq, cm^{-1}
$[Rh_2(CO)_2(O_2CCH_3)(DPM)_2]PF_6$	1986 (vs), 1962 (vs) [2000 (vs), 1985 (sh)]	1945 (vs), 1931 (vs)	1532 (m) (O_2CCH_3)
$[Rh_2(CO)_2(O_2CCH_3)(DAM)_2]PF_6$	1985 (vs), 1970 (vs) [1997 (vs), 1983 (sh)]	1942 (vs), 1930 (vs)	1523 (m) (O_2CCH_3)
$[Rh_2(CO)_2(O_2CC_2H_5)(DAM)_2]PF_6$	1980 (vs), 1966 (vs) [1999 (vs), 1984 (vs)]	1944 (vs), 1932 (vs)	1520 (m) ($O_2CC_2H_5$)
$[Rh_2(CO)_2(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DPM)_2]PF_6$	2046 (vs), 1735 (m) [2063 (vs), 1737 (s)]	2000 (vs), 1697 (s)	1713 (m), 1692 (m) (CO_2CH_3); 1574 (w) (O_2CCH_3)
$[Rh_2(CO)_2(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DAM)_2]PF_6$	2046 (vs), 1736 (m) [2063 (vs), 1737 (s)]	2000 (vs), 1698 (s)	1712 (m), 1695 (m) (CO_2CH_3); 1575 (w) (O_2CCH_3)
$[Rh_2(CO)_2(CH_3O_2CC_2CO_2CH_3)(O_2CC_2H_5)(DAM)_2]PF_6$	2050 (vs), 1737 (m) [2062 (s), 1742 (m)]	2000 (vs), 1695 (s)	1719 (m), 1697 (m) (CO_2CH_3); 1575 (w) ($O_2CC_2H_5$)
$[Rh_2(CO)_2(CF_3C_2CF_3)(O_2CCH_3)(DPM)_2]PF_6$	2045 (vs), 1752 (m) [2071 (vs), 1745 (s)]	2011 (vs), 1706 (s)	1603 (w) (O_2CCH_3)
$[Rh_2(CO)_2(CF_3C_2CF_3)(O_2CCH_3)(DAM)_2]PF_6$	2048 (vs), 1754 (m) [2071 (vs), 1746 (s)]	2010 (vs), 1714 (s)	1601 (w) (O_2CCH_3)
$[Rh_2(CO)_2(CF_3C_2CF_3)(O_2CC_2H_5)(DAM)_2]PF_6$	2060 (vs), 1756 (s) [2067 (s), 1747 (s)]	2014 (vs), 1717 (s)	1602 (w) ($O_2CC_2H_5$)
$[Rh_2(CO)(P(OCH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DPM)_2]PF_6$	1712 (sh) [1715 (sh)]	1674 (m)	1708 (s), 1694 (m) (CO_2CH_3)
$[Rh_2(CO)(P(OCH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DAM)_2]PF_6$	1712 (sh) [1714 (sh)]	1673 (s)	1709 (vs), 1694 (m) (CO_2CH_3)
$[Rh_2(CO)(P(OCH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DPM)_2]PF_6$	1715 (s) [1717 (s)]	1686 (s)	
$[Rh_2(CO)(P(OCH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DAM)_2]PF_6$	1719 (sh), 1713 (s) [1721 (s)]	1681 (s)	
$[Rh_2(CO)(CNC(CH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DPM)_2]PF_6$	1715 (sh) [1720 (sh)]	1678 (s)	2167 (s) [2176 (s)] (C≡N); 1710 (s), 1690 (m) (CO_2CH_3)
$[Rh_2(CO)(CNC(CH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DAM)_2]PF_6$	1710 (sh) [1720 (sh)]	1678 (s)	2169 (s) [2174 (s)] (C≡N); 1707 (s), 1687 (m) (CO_2CH_3)
$[Rh_2(CO)(CNC(CH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DPM)_2]PF_6$	1740 (m) [1725 (s)]	1700 (s)	2171 (vs) [2183 (s)] (C≡N)
$[Rh_2(CO)(CNC(CH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DAM)_2]PF_6$	1740 (s) [1720 (s)]	1703 (s)	2170 (s) [2182 (s)] (C≡N)
$[Rh_2(CNC(CH_3)_3)_4(CH_3O_2CC_2CO_2CH_3)(DPM)_2](B(C_6H_5)_4)_2$			2183 (sh), 2163 (s), 2143 (sh) [2188 (m), 2170 (vs), 2144 (m)] (C≡N); 1704 (m), 1678 (m) (CO_2CH_3)
$[Rh_2(CNC(CH_3)_3)_4(CF_3C_2CF_3)(DPM)_2](B(C_6H_5)_4)_2$			2177 (s), 2158 (s) [2181 (s), 2161 (s)] (C≡N)

[a] Unbracketed values in Nujol mulls, bracketed values in CH_2Cl_2 solution. Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table III. NMR Chemical Shifts[a]

complex	τ(H)[b]	assignt	δ(^{13}C)[c]	assignt	T, °C
$[Rh_2(CO)_2(O_2CCH_3)(DPM)_2]PF_6$	9.26 (s) (3 H)	O_2CCH_3	189.8 (dm) ($^1J_{Rh-C} = 73.2$)	CO (term)	28
	6.30 (m) (4 H)	CH_2			
$[Rh_2(CO)_2(O_2CCH_3)(DAM)_2]PF_6$	9.35 (s) (3 H)	O_2CCH_3	188.2 (d) ($^1J_{Rh-C} = 67.9$)	CO (term)	28
	6.18, 6.83 (AB) (4 H)	CH_2			
$[Rh_2(CO)_2(O_2CC_2H_5)(DAM)_2]PF_6$	8.83 (q) (2H), 9.02 (t) (3 H)	$O_2C-CH_2-CH_3$	188.7 (d) ($^1J_{Rh-C} = 67.9$)	CO (term)	28
	6.40, 6.79 (AB) (4 H)	CH_2			
$[Rh_2(CO)_2(O_2CCH_3)(CH_3O_2CC_2CO_2CH_3)(DPM)_2]PF_6$	8.56 (s) (3 H)	O_2CCH_3	190.1 (dt) ($^1J_{Rh-C} = 53.2$, $^2J_{P-C} = 10.3$)	CO (term)	−43
	6.67 (s) (3 H), 8.19 (s) (3 H)	CO_2CH_3	208.6 (m) ($^1J_{Rh-C} = 41.0$, $^1J_{Rh'-C} = 20.5$;		
	6.20 (m) (4 H)	CH_2	$^2J_{P-C} = 7.9$, $^2J_{P'-C} = 3.4$)	CO (br)	
$[Rh_2(CO)_2(O_2CCH_3)(CH_3O_2CC_2CO_2CH_3)(DAM)_2]PF_6$	8.58 (s) (3 H)	O_2CCH_3	189.2 (d) ($^1J_{Rh-C} = 51.8$)	CO (term)	28
	6.57 (s) (3 H), 8.11 (s) (3 H)	CO_2CH_3	205.2 (dd) ($^1J_{Rh-C} = 40.0$, $^1J_{Rh'-C} = 20.5$)	CO (br)	
	6.05, 7.12 (AB) (4 H)	CH_2			
$[Rh_2(CO)_2(O_2CC_2H_5)(CH_3O_2CC_2CO_2CH_3)(DAM)_2]PF_6$	8.28 (q) (2 H), 9.53 (t) (3 H)	$O_2C-CH_2-CH_3$	188.5 (d) ($^1J_{Rh-C} = 52.3$)	CO (term)	−52
	6.56 (s) (3 H), 8.09 (s) (3 H)	CO_2CH_3	206.0 (dd) ($^1J_{Rh-C} = 39.7$, $^1J_{Rh'-C} = 21.0$)	CO (br)	
	6.04, 7.11 (AB) (4 H)	CH_2			
$[Rh_2(CO)_2(O_2CCH_3)(CF_3C_2CF_3)(DPM)_2]PF_6$	9.27 (s) (3 H)	O_2CCH_3	188.0 (dm) ($^1J_{Rh-C} = 52.3$)	CO (term)	−38
			202.0 (m)	CO (br)	
$[Rh_2(CO)_2(O_2CCH_3)(CF_3C_2CF_3)(DAM)_2]PF_6$	8.32 (s) (3 H)	O_2CCH_3	188.2 (d) ($^1J_{Rh-C} = 51.5$)	CO (term)	28
	6.26, 6.91 (AB) (4 H)	CH_2	199.5 (dd) ($^1J_{Rh-C} = 39.9$, $^1J_{Rh'-C} = 21.1$)	CO (br)	
$[Rh_2(CO)_2(O_2CC_2H_5)(CF_3C_2CF_3)(DAM)_2]PF_6$	6.51 (q) (2 H), 8.86 (t) (3 H)	$O_2C-CH_2-CH_3$	187.3 (d) ($^1J_{Rh-C} = 52.2$)	CO (term)	−52
	6.25, 6.90 (AB) (4 H)	CH_2	200.0 (dd) ($^1J_{Rh-C} = 40.5$, $^1J_{Rh'-C} = 21.0$)	CO (br)	
$[Rh_2(CO)(P(OCH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DPM)_2]PF_6$	8.51 (s) (3 H)	O_2CCH_3	210.2 (m) ($^1J_{Rh-C} = 38.5$, $^1J_{Rh'-C} = 23.8$;	CO (br)	28
	6.78 (s) (3 H), 8.19 (s) (3 H)	CO_2CH_3	$^2J_{P-C} = 8.1$, $^2J_{P'-C} = 5.2$)		
	6.43 (m) (4 H)	CH_2			
	6.75 (d) (9 H) ($J_{P-H} = 10.4$)	$P-O-CH_3$			
$[Rh_2(CO)(P(OCH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DAM)_2]PF_6$	8.49 (s) (3 H)	O_2CCH_3	204.3 (dd) ($^1J_{Rh-C} = 37.6$, $^1J_{Rh'-C} = 23.4$)	CO (br)	28
	6.74 (s) (3 H), 8.07 (s) (3 H)	CO_2CH_3			
	6.23, 7.45 (AB) (4 H)	CH_2			
	6.74 (d) (9 H) ($J_{P-H} = 10.4$)	$P-O-CH_3$			
$[Rh_2(CO)(P(OCH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DPM)_2]PF_6$	8.30 (s) (3 H)	O_2CCH_3	201.3 (m) ($^1J_{Rh-C} = 39.1$, $^1J_{Rh'-C} = 24.4$;	CO (br)	28
	6.42 (m) (4 H)	CH_2	$^2J_{P-C} = 6.8$, $^2J_{P'-C} = 5.8$)		
	6.82 (d) (9 H) ($J_{P-H} = 10.4$)	$P-O-CH_3$			
$[Rh_2(CO)(P(OCH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DAM)_2]PF_2$	8.26 (s) (3 H)	O_2CCH_3	200.6 (dd) ($^1J_{Rh-C} = 38.1$, $^1J_{Rh'-C} = 24.4$)	CO (br)	28
	6.43, 7.22 (AB) (4 H)	CH_2			
	6.79 (d) (9 H) ($J_{P-H} = 10.7$)	$P-O-CH_3$			
$[Rh_2(CO)(CNC(CH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DPM)_2PF_6$	8.91 (s) (9 H)	$C(CH_3)_3$	209.9 (m) ($^1J_{Rh-C} = 37.5$, $^1J_{Rh'-C} = 22.8$;	CO (br)	28
	8.53 (s) (3 H)	O_2CCH_3	$^2J_{P-C} = 8.0$, $^2J_{P'-C} = 5.3$)		
	6.40 (m) (4 H)	CH_2			
	6.79 (s) (3 H), 8.21 (s) (3 H)	CO_2CH_3			
$[Rh_2(CO)(CNC(CH_3)_3)(CH_3O_2CC_2CO_2CH_3)(O_2CCH_3)(DAM)_2]PF_6$	8.90 (s) (9 H)	$C(CH_3)_3$	207.0 (dd) ($^1J_{Rh-C} = 37.0$, $^1J_{Rh'-C} = 23.0$)	CO (br)	28
	8.52 (s) (3 H)	O_2CCH_3			
	6.72 (s) (3 H), 8.02 (s) (3 H)	CO_2CH_3			
	6.25, 7.27 (AB) (4 H)	CH_2			
$[Rh_2(CO)(CNC(CH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DPM)_2]PF_6$	8.97 (s) (9 H)	$C(CH_3)_3$	203.4 (m)	CO (br)	28
	8.35 (s) (3 H)	O_2CCH_3			
	6.35 (m) (4 H)	CH_2			
$[Rh_2(CO)(CNC(CH_3)_3)(CF_3C_2CF_3)(O_2CCH_3)(DAM)_2]PF_6$	8.97 (s) (9 H)	$C(CH_3)_3$	200.7 (dd) ($^1J_{Rh-C} = 37.6$, $^1J_{Rh'-C} = 23.0$)	CO (br)	28
	8.33 (s) (3 H)	O_2CCH_3			
	6.40, 7.12 (AB) (4 H)	CH_2			
$[Rh_2(CNC(CH_3)_3)_4(CH_3O_2CC_2CO_2CH_3)(DPM)_2](B(C_6H_5)_4)_2$	8.63 (s) (9 H), 9.07 (s) (9 H)	$C(CH_3)_3$			
	7.03 (s) (6 H)	CO_2CH_3			
	5.82 (m) (4 H)	CH_2			
$[Rh_2(CNC(CH_3)_3)_4(CF_3C_2CF_3)(DPM)_2](B(C_6H_5)_4)_2$	8.76 (s) (9 H), 9.12 (s) (9 H)	$C(CH_3)_3$			
	5.95 (m) (4 H)	CH_2			

[a] Recorded in CD_2Cl_2 solution. Key: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets: dt, doublet of triplets; dm, doublet of multiplets; m, multiplet; AB, second-order AB spin system; term, terminal; br, bridge. All J values are given in hertz. [b] Referenced to tetramethylsilane (internal, τ 10.0). The number in parentheses indicates the number of protons. [c] Referenced to tetramethylsilane (external, δ 0.0) and positive downfield.

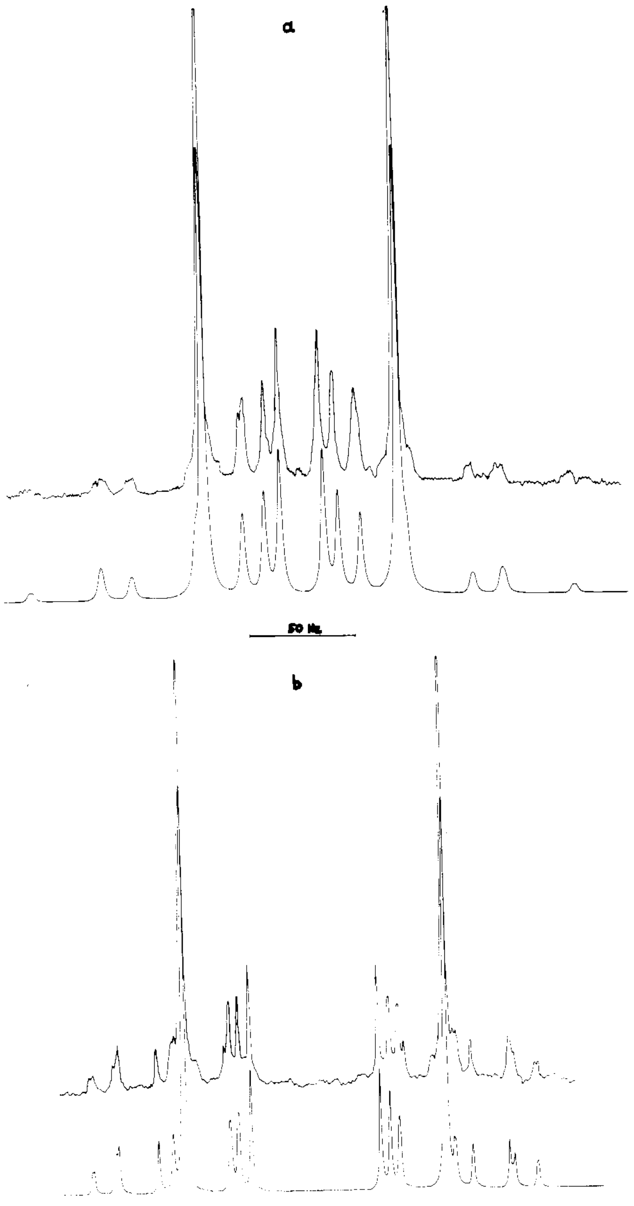


Figure 1. Observed and calculated $^{31}P\{^1H\}$ NMR spectrum of (a) $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2CCH_3)(DPM)_2]PF_6$ at −70 °C under CO and (b) $[Rh_2(CO)_2(\mu\text{-}O_2CCH_3)(DPM)_2]PF_6$ (**1**).

bridging the two metal atoms.[5] (The lower energy band expected for the carboxylate group in these complexes as well as those discussed later was obscured by other ligand absorptions.) The $^{13}C\{^1H\}$ NMR spectra of **2** and **3** show a sharp doublet resonance in the terminal carbonyl region (Table III), which indicates that the carbonyl groups are equivalent. For **1** the resonance is a doublet of multiplets as was found[1] for $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$. Here the additional complexity is due to the presence of coupling to phosphorus, but again, equivalence of the two terminal carbonyl groups is indicated. Further confirmation of a symmetrical structure for **1** comes from its $^{31}P\{^1H\}$ NMR spectrum, which is a symmetric second-order pattern very similar to that observed previously[1] for $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ and several of its derivatives. As before, it has been possible to analyze this spectrum as an AA'A''A'''XX' spin system with $\delta(P) = 18.2$ and $^1J_{\mathrm{Rh-P}} = 125.4$, $^2J_{\mathrm{P-Rh-P}} = 340$, $^2J_{\mathrm{P-C-P}} = 62.8$, $^4J_{\mathrm{P-P}} = 7.7$, $^xJ_{\mathrm{Rh'-P}} = 0.6$, and $^1J_{\mathrm{Rh-Rh'}} = 0.7$ Hz (Figure 1b). Once again, the value of $^2J_{\mathrm{P-Rh-P}}$ is not well determined because of the insensitivity of the major features of the spectrum to this parameter. Nonetheless, although this may not be a unique solution, the derived coupling constants are reasonable and consistent with the proposed structure (see Scheme I).

As was found for $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]^+$, **1**–**3** show rapid CO exchange in the presence of excess CO. This has been determined by the preparation of derivatives 90% enriched in ^{13}CO (see Table II here and below for the carbonyl absorptions of the isotopically labeled complexes) and by the observation by a single broad resonance in the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of each complex at 30 °C. At −70 °C, the $^{13}C\{^1H\}$ NMR spectrum of **1** in the presence of ^{13}CO shows well-defined multiplet resonances attributable to terminal and bridging carbonyl ligands (Table III), which closely resemble those found[1] for $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$. The $^{31}P\{^1H\}$ NMR spectrum of the unlabeled complex (Figure 1a) remains a symmetrical AA'A''A'''XX' pattern ($\delta(P) = 30.0$; $^1J_{\mathrm{Rh-P}} = 94.6$, $^2J_{\mathrm{P-Rh-P}} = 320$, $^2J_{\mathrm{P-C-P}} = 83.0$, $^4J_{\mathrm{P-P}} = 29.5$, $^xJ_{\mathrm{Rh'-P}} = -1.4$, $^1J_{\mathrm{Rh-Rh'}} = 1.0$ Hz), thus confirming that the species present can be formulated as $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}O_2CCH_3)(DPM)_2]PF_6$. For **2** and **3** on the other hand no significant change in the ^{13}C NMR spectrum is noted down to the low-temperature limit of the spectrometer (−80 °C), indicating that CO exchange is still rapid. Although the μ-CO adduct of **1** appears stable at −70 °C and can be precipitated at this temperature, it rapidly loses CO on warming and reverts to **1**. The lability of the bridging carbonyl ligand is significantly greater in these carboxylate-bridge complexes as compared with that of chloro-bridged dimers studied earlier. This increased lability is probably the result of a combination of electronic and steric factors. Thus on replacement of the bridging chloride by a bridging carboxylate ligand, a lower electron density on the metals and a greater metal–metal separation could be expected, both of which would reduce the ability of CO to bind in a bridging position.

Complexes **1**–**3** react readily with the electronegatively substituted acetylenes hexafluorobut-2-yne and dimethyl acetylenedicarboxylate to yield 1:1 adducts analyzing as $[Rh_2(CO)_2(O_2CR')(RCCR)(L_2)_2]PF_6$ ($R' = CH_3$, $R = CO_2CH_3$, L_2 = DPM (**4**), DAM (**5**); $R' = C_2H_5$, $R = CO_2CH_3$, L_2 = DAM (**6**); $R' = CH_3$, $R = CF_3$, L_2 = DPM (**7**), DAM (**8**); $R' = C_2H_5$, $R = CF_3$, L_2 = DAM (**9**)) (Scheme I). The infrared spectra in the carbonyl region (Table II) indicate the presence of terminal and bridging carbonyl ligands. In addition, the band attributed to the bridging carboxylate group in **1**–**3** has shifted to higher energy and now appears in the region characteristic of a monodendate carboxylate group.[5] The conductivity data show that these complexes also behave as 1:1 electrolytes, which indictes that the carboxylate group must remain coordinated.

The $^{13}C\{^1H\}$ NMR spectra of the arsine complexes **5**, **6**, **8**, and **9** are all very similar (Table III). Each consists of two resonances of equal intensity, namely, a doublet in the terminal carbonyl region and a doublet of doublets in the bridging carbonyl region. The appearance of the latter resonance indicates that the two rhodium atoms are not equivalent. The $^{13}C\{^1H\}$ NMR spectrum of the phosphine complex **4** consists of a doublet of triplets for the terminal carbonyl ligand and a complex multiplet for the bridging carbonyl. Although the resolution of this resonance was only fair, it nevertheless proved possible to simulate the multiplet pattern by using two different rhodium–carbon and two different phosphorus–carbon coupling constants (Table III), which confirms that here also the two sides of the molecule are not equivalent (see Figure 2 for a typical example). In contrast to our earlier results for $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$,[1] no coupling between bridging and terminal carbonyl groups was observed. Because

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(5) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 232.

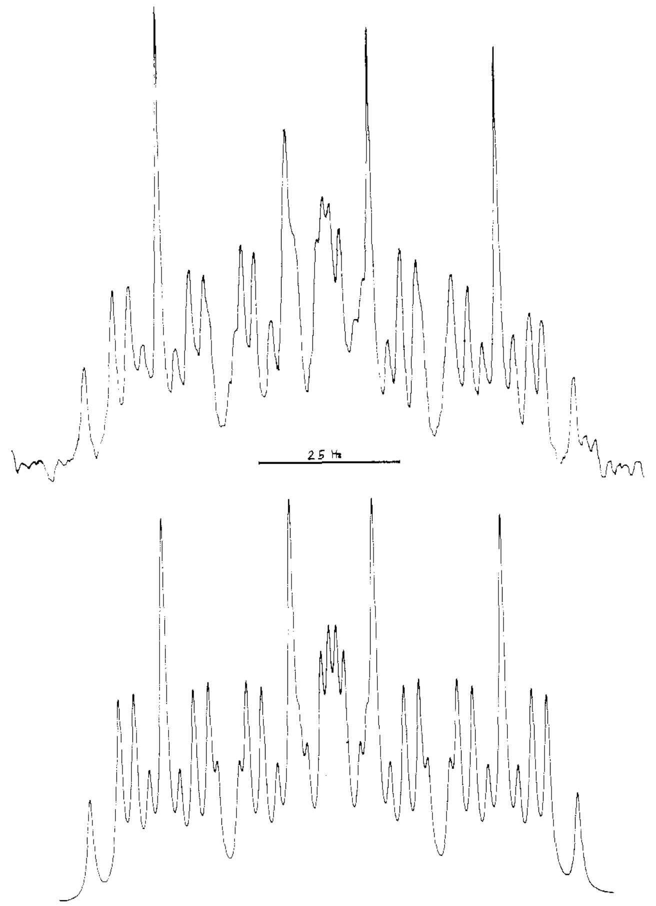
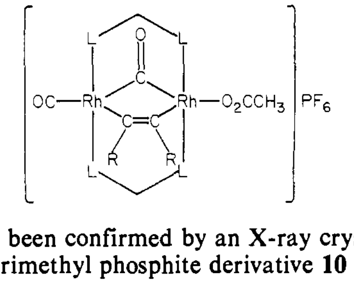


Figure 2. Observed and calculated $^{13}C\{^1H\}$ NMR spectrum of $[Rh_2(CNC(CH_3)_3)(\mu\text{-}CO)(\mu\text{-}H_3CO_2CC_2CO_2CH_3)(O_2CCH_3)(DPM)_2]PF_6$ (**14**).

of the low solubility of **7**, the bridging carbonyl resonance had insufficient resolution to warrant analysis. However, the close similarity of the infrared spectrum of this complex to those for the other hexafluorobut-2-yne adducts as well as to that for **4** leaves little doubt that **7** has the same structure. The $^{31}P\{^1H\}$ NMR spectra of **4** (Figure 3) and **7** are complex second-order patterns spread over a range of ca. 8–20 ppm downfield from phosphoric acid. Extensive attempts to simulate these spectra met with only limited success, which appears due in part to the relative intensitivity of the major features of the spectra of the magnitude of $^2J_{P-Rh-P}$. Nevertheless it was clear from the attempts at simulation that the general features could be generated by treating them as AA′BB′XY spin systems with values of $^1J_{Rh-P}$ and $^2J_{P-Rh-P}$ comparable to those found here and earlier[1] for the symmetrical complexes and with chemical shift differences between the two sets of phosphorus atoms of ca. 2–5 ppm. These results thus further support the conclusion that, in these complexes, the two sides are not equivalent. The structure for **4–9** that is most consistent with the spectroscopic and conductivity data is



This has now been confirmed by an X-ray crystal structure study of the trimethyl phosphite derivative **10** (current $R = 0.06$).[15]

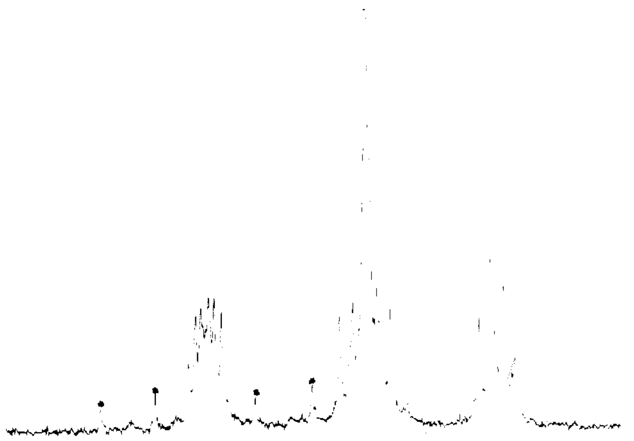


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2(CO)(\mu\text{-}CO)(\mu\text{-}H_3CO_2CC_2CO_2CH_3)(O_2CCH_3)(DPM)_2]PF_6$ (**4**). The starred peaks are the "fold-over" of a portion of the PF_6^- signal.

The X-ray crystal structure of the related species $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)(DPM)_2]$[6] appeared while this work was in progress, and the inner coordination spheres of the two metals are essentially the same as found in **10**. Also reported in this paper was the complex $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}CF_3C{=}CCF_3)(DPM)_2]$,[6] which appears from the data provided to be identical with that which we prepared earlier.[2]

It is of interest to compare our acetylene adducts with those reported by Cowie.[6] Most notable are the higher frequencies observed here for the bridging carbonyl absorption and the distinctly different rhodium–carbon coupling constants. While these differences could indicate a decidedly asymmetric bonding of the bridging carbonyl, conventional electron counting favors a "ketonic" formulation.[6,7] On this basis, the higher stretching frequency for this ligand in our systems can be rationalized as being due to the combined electron-withdrawing effects of a formally positive metal atom and the terminal carbonyl ligand. This view is supported by the observation that on substitution of the terminal carbonyl by weaker π-acid ligands (vide infra) the stretching frequency of the bridging carbonyl is lowered. Also with this formulation, the different electronic characters of the two metal atoms (one positive and one neutral) could account for the different rhodium–carbon coupling constants.

Previously, we have reported on the coupling of perfluorobut-2-yne and carbon monoxide when bound to rhodium to give rhodacyclobutenone and rhodacyclopentenedione derivatives.[8] The cis arrangement of a carbonyl group and a metal–carbon bond in complexes **4–9** suggested the posssibility of CO "insertion" to give a three-carbon bridge. The desired reaction does not, however, appear to occur at least under moderate conditions. Thus the complexes are recovered unchanged after refluxing for several hours in dichloromethane, and on reaction with either *tert*-butyl isocyanide or trimethyl phosphite only substitution of the terminal carbonyl group occurs to give the complexes **10–17** (Scheme I). In these reactions the isocyanide appears better able to replace the carbonyl group as complete reaction could be achieved after stirring overnight at room temperature. Under the same conditions with trimethyl phosphite, significant quantities of a species containing a terminal carbonyl remained. However, when it was conducted at reflux, complete substitution could be achieved with this ligand as well. The fact that the terminal carbonyl group in **4–9** is not lost in the absence of added ligand

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

(7) Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543.

(8) Mague, J. T.; Nutt, M. O.; Gause, E. H. *J. Chem. Soc., Dalton Trans.* **1973**, 2578.

suggests that these reactions proceed by associative attack adjacent to this carbonyl. The possibility that these complexes could be susceptible to nucleophilic attack at this site has been previously noted.[7]

The observation of 1:1 electrolyte behavior for **10**–**17** indicates that the acetate remains coordinated, and although we could not unequivocally identify infrared bands due to this moiety, we presume it to be bound as a monodentate ligand here as well. This is based on the very close similarity of all other spectroscopic data for **10**–**17** to those for the parent species **4**–**9**, which strongly suggests that the same basic structure is retained. The infrared spectra show only a bridging carbonyl absorption shifted to somewhat lower energy from the parent species in keeping with the lower π-acid character of isocyanide or phosphite as compared with that of a terminal carbonyl. In **14**–**17** a single absorption characteristic of a terminal isocyanide ligand is also present. The proton NMR spectra of **10**–**17** differ from their parent species only in the appearance of additional resonances associated with the new ligands. Similarly the $^{13}C\{^1H\}$ spectra of the bridging carbonyl ligands (Figure 2) differ only slightly in appearance, chemical shifts, and coupling constants from those of their respective precursors (Table III) although for **16** the resolution was insufficient for a full simulation of the spectrum to be made.

The $^{31}P\{^1H\}$ NMR spectra of the isocyanide complexes **14** and **17** also closely resemble those of **4** and **7**, and although their complete simulation could not be accomplished, it is clear from these attempts that these too are unsymmetrical six-spin systems. The $^{31}P\{^1H\}$ NMR spectrum of the phosphite complex **11** appears as a sharp doublet at 117.2 ppm ($^1J_{Rh-P} = 168.4$ Hz), which compares favorably with values observed previously.[9] For **13**, the ^{31}P NMR spectrum consists of a doublet of quartets, indicating the presence of coupling to a trifluoromethyl group (δ(P) 111.3, $^1J_{Rh-P} = 166.5$, $^4J_{P-F} = 10.2$ Hz). A similar long-range phosphorus–fluorine coupling has been observed previously in $[Rh(C(CF_3){=}CHCF_3)(P(C_6H_5)_3)_2PF_3]$.[10]

In the region associated with the DPM ligand, the ^{31}P NMR spectra of **10** and **12** differ from those of **4** and **7** primarily in additional splittings of the original multiplets by the phosphite ligand. In the phosphite region, that of **10** shows a well-resolved double triplet of triplets centered at 118.2 ppm with $^1J_{Rh-P} = 173.3$, $^2J_{P-P'} = 40.2$, and $J_{P-P''} = 2.7$ Hz where P′ and P″ represent the phosphorus atoms of the DPM ligand adjacent to and remote from the phosphite ligand, respectively. For **12** the phosphite resonance appears as a poorly resolved doublet of multiplets at 108.3 ppm with $^1J_{Rh-P} = 170.9$ and $^2J_{P-P'} = 42.7$ Hz as the only couplings that could be determined. The relatively low solubility of this complex made it difficult to obtain a better resolved spectrum, but the poor resolution may also be due to additional coupling to the neighboring trifluoromethyl group.

The complex $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$ also reacts slowly with dimethyl acetylenedicarboxylate and hexafluorobut-2-yne to yield the adducts **18** and **19**, respectively, both of which analyze as $[Rh_2(CNC(CH_3)_3)_4(\text{acetylene})(DPM)_2](B(C_6H_5)_4)_2$ and behave as 1:2 electrolytes. The proton NMR spectra of both complexes show two signals of equal intensity for the *tert*-butyl groups while for **18** a single resonance is observed for the carboxymethyl groups. The $^{31}P\{^1H\}$ NMR spectra of both complexes are symmetrical patterns centered at 9.2 and 2.6 ppm, respectively, downfield from external phosphoric acid. These closely resemble the AA′A″A‴XX′ patterns observed previously[1] for the CO and SO_2 adducts of $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$, and the separation of the major peaks (95.8 Hz for **18** and 93.0 Hz for **19**) also compares well with the observed in those adducts (a full analysis was not performed because of considerable overlap of the weaker lines, which made it impossible to make unequivocal assignments). It is clear from the NMR data that the acetylene molecule is symmetrically bound to both metals on one face of the dimer, and the similarity of the major peak separation to that seen in $[Rh_2(\mu\text{-}L)(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$ (L = CO, SO_2) suggests a similar structure, which implies that the carbon–carbon axis parallels the metal–metal axis as in the complexes described above. However, we cannot at this point exclude the perpendicular orientation as has been found for $[Co_2(CO)_4(Ph_2C_2)(DPM)]$,[11] $[Co_2(CO)_2(Ph_2C_2)(DAM)_2]$,[11] and $[Rh_2(PF_3)_4(Ph_2C_2)(PPh_3)_2]$,[12] and a definite answer must await the completion of a planned X-ray crystal structure determination.

On contact with CO, the brownish orange dichloromethane solutions of **18** and **19** immediately become bright yellow, and yellow crystals can be obtained by precipitation with diethyl ether. Also, the brownish pink crystals of **19** immediately become pale yellow on contact with CO but revert to their original color on standing for several days. Although these color changes are very similar to those observed on reaction of CO with $[Rh_2(CNC(CH_3)_3)_4(L_2)_2]^{2+}$ or $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]^+$ (L_2 = DPM, DAM), no firm infrared or NMR evidence for coordination of carbon monoxide to **18** or **19** was obtained either in solution or in the solid state nor did it appear that displacement of the acetylene moiety had occurred. The fact that the acetylene is not displaced by CO is consistent with it being bound as a bridging vinylidene group as suggested earlier but does not prove that this is the structure. It is difficult to account for the rather significant color change that occurs on exposure of **18** and **19** to CO without postulating the formation of a new species, but with the data presently in hand we cannot say what it might be. Work is continuing to explore this system.

We have previously reported on the ability of $[Rh_2(CO)_2(\mu\text{-}Cl)(DAM)_2]PF_6$ to catalyze the hydrogenation of methylphenylacetylene to *cis*-β-methylstyrene.[13] Having in hand the acetylene adducts described above, we have investigated the reactivity of these complexes toward hydrogen. Initially we found that **1** was inactive as a catalyst for the hydrogenation of dimethyl acetylenedicarboxylate in dichloromethane solution at 25 °C and 20 psi hydrogen although the adduct **4** was clearly present in solution. On the other hand, when a suspension of **4** in dichloromethane is treated with hydrogen under the same conditions but in the absence of excess acetylene, the solid dissolves over a period of about 1 h to give a dark brownish red solution. Removal of the solvent and extraction with ether afforded a small amount of a liquid tentatively identified by NMR as dimethyl succinate. An infrared spectrum of the solid remaining after the extraction showed carbonyl absorptions in the 1950–2000-cm^{-1} region, which appeared to be very similar to those observed for **1**. We have thus defined a possible intermediate (**4**) in the hydrogenation of acetylenes by A-frame complexes although it is disappointing that no catalytic hydrogenation has yet been observed in the present system. Work is continuing in this area, and

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[9] Pregosin, P. S.; Kunz, R. W. "NMR, Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1979; Vol. 16.

[10] Hosseini, H. E.; Nixon, J. F.; Poland, J. S. *J. Organomet. Chem.* **1979**, *164*, 107.

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[12] Bennett, M. A.; Johnson, R. W.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *Inorg. Chem.* **1976**, *15*, 97.

[13] Mague, J. T.; DeVries, S. H., Paper No. 23, presented at the Biennial Inorganic Chemistry Symposium, Guelph, Ontario, Canada, 1980.

[14] Castellano, S.; Bothner-By, A. R. *J. Chem. Phys.* **1964**, *41*, 3863.

[15] Mague, J. T., to be submitted for publication in *Inorg. Chem.*

1638 *Inorg. Chem.* **1982**, *21*, 1638-1640

further results will be reported in a subsequent publication.

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Registry No. **1**, 80461-63-8; **2**, 80448-48-2; **3**, 80448-50-6; **4**, 80448-52-8; **5**, 80448-54-0; **6**, 80448-56-2; **7**, 80448-58-4; **8**, 80448-60-8; **9**, 80448-62-0; **10**, 80448-64-2; **11**, 80461-65-0; **12**, 80448-66-4; **13**, 80448-68-6; **14**, 80448-70-0; **15**, 80448-72-2; **16**, 80448-74-4; **17**, 80448-76-6; **18**, 80461-67-2; **19**, 80461-69-4; $[Rh_2(CO)_2(\mu\text{-Cl})(DPM)_2]PF_6$, 80448-77-7; $[Rh_2(CO)_2(\mu\text{-Cl})(DAM)_2]PF_6$, 74965-10-9; $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$, 74977-80-3.

Supplementary Material Available: Tables I and IV giving analytical and conductance data, respectively (2 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Laboratory,
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Dicationic Tetrakis(triphenylphosphine)palladium(II) and Tetrakis(triphenyl phosphite)palladium(II) Complexes

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The synthesis and properties of the cationic palladium(II) complexes are described. Dicationic $[Pd(PPh_3)_4](X)_2$ (X = BF_4^-, PF_6^-) and $[Pd(P(OPh)_3)_4](PF_6)_2$ have been prepared by the reaction of $Pd(PPh_3)_4$ with CPh_3X (X = BF_4^-, PF_6^-). A pentacoordinated Pd(II) complex of the heterocyclic ligand 1,10-phenanthroline, $[Pd(1,10\text{-phen})_2(PPh_3)](X)_2$, was obtained from the reaction of $[Pd(PPh_3)_4](X)_2$ with 1,10-phen. Monocationic $[Pd(CH_3COCHCO\text{–}R)(PPh_3)_2](X)$ (R = Me, OMe) has been isolated from the reaction of $Pd(PPh_3)_4$ with CPh_3X in the presence of acetylacetone or methyl acetoacetate. Likely structures and some features for these new complexes are proposed from ^{1}H NMR and IR spectrometry.

Although the cationic platinum(II) acetylacetonate complex $[Pt(acac)(PPh_3)](BF_4)$ has been prepared,[1] its palladium analogue has been elusive. Recently, the preparation of cationic hydride complexes of the type $[Pt(PPh_3)_3H](X)$ (X = ClO_4^-, HSO_4^-, or BF_4^-) by the oxidative-addition reaction of $Pt(PPh_3)_4$ has been reported.[2] However, a square-planar Pd(II) complex having only unidentate phosphine[3,4] or phosphite ligands has not yet been reported.

I have succeeded in isolating the tetrakis(triphenylphosphine)palladium(II) complex $[Pd(PPh_3)_4](X)_2$ (X = BF_4^-, PF_6^-) and its phosphite analogue $[Pd(P(OPh)_3)_4](PF_6)_2$. Also the pentacoordinated complex $[Pd(1,10\text{-phen})_2(PPh_3)](X)_2$ was isolated. In this paper, the preparation and some reactions for these complexes are described.

Experimental Section

All the solvents were purified by the distillation of commercial solvents over Na or $CaCl_2$. All the reactions were carried out in vacuo or under nitrogen, but the products are thermally stable and air stable, and isolations were carried out in air.

Tetrakis(triphenylphosphine)palladium(0) was prepared by a literature procedure[5] or by the reduction of $PdCl_2(PPh_3)_2$ (4.4 g) with sodium borohydride in 130 mL of hot EtOH containing 5 g of PPh_3. The yellow suspended solution slowly turned to canary yellow. The reaction was completed in 10 min, and the solution was cooled in cold water. Then the canary yellow solids were filtered and washed with water, EtOH, and heptane (yield 83%).

Tetrakis(triphenyl phosphite)palladium(0) was prepared by following the procedure of the preparation of tetrakis(triphenyl phosphite)platinum(0).[6] $Pd(PPh_3)_4$, 1.3 g, was dissolved in 15 mL of benzene, and an excess amount of $P(OPh)_3$ (~2 g) was added. The yellow solution slowly lost its color. The transformation to $Pd(P(OPh)_3)_4$ was completed in 6 h, the solvent was removed under reduced pressure to about half of the total volume, and addition of pentane to the solution gave white crystals (yield 100%).

Tetrakis(triphenylphosphine)palladium(II) Complex, $[Pd(PPh_3)_4](BF_4)_2\cdot(CH_3)_2CO$. A 2.0-g quantity of $Pd(PPh_3)_4$ was dissolved in 15 mL of benzene, and an acetone solution of CPh_3BF_4, 1.4 g in 20 mL, was added to the complex solution. Then the mixed solution was left agitating for 6 h. The solvent was removed under reduced pressure to one-fifth of the total volume. Addition of diethyl ether to the residue solution gave pale yellow crystals (2.2 g, 90%). Anal. Calcd for $[Pd(PPh_3)_4](BF_4)_2\cdot(CH_3)_2CO$: C, 64.93; H, 4.80. Found: C, 64.32; H, 4.43. IR (Nujol mull): ν(CO) of the acetone of solvation 1710 cm^{-1} (strong). The PF_6^- salt was prepared analogously, giving yellow crystals (61%). Anal. Calcd for $[Pd(PPh_3)_4](PF_6)_2\cdot(CH_3)_2CO$: C, 59.91; H, 4.43. Found: C, 60.05; H, 4.58. IR (Nujol mull): ν(CO) of the acetone of solvation 1710 cm^{-1} (strong).

Tetrakis(triphenyl phosphite)palladium(II) Complex, $[Pd(P(OPh)_3)_4](PF_6)_2\cdot(CH_3)_2CO$. A 1.6-g of quantity of $Pd(P(OPh)_3)_4$ was dissolved in 15 mL of benzene, and an acetone solution of CPh_3PF_6, 0.97 g in 20 mL, was added. The reaction was completed in 24 h, the solvents of the solution were removed under reduced pressure to one-fifth of the total volume, and addition of pentane to the residue solution gave white crystals (0.8 g, 50%). Anal. Calcd for $[Pd(P(OPh)_3)_4](PF_6)_2\cdot(CH_3)_2CO$: C, 57.46; H, 4.24. Found: C, 57.40; H, 4.99. IR (Nujol mull): ν(CO) of the acetone of solvation 1723 cm^{-1}.

Bis(1,10-phenanthroline)(triphenylphosphine)palladium(II) Complex, $[Pd(1,10\text{-phen})_2(PPh_3)](BF_4)_2\cdot(CH_3)_2CO$. A 0.7-g of quantity of $[Pd(PPh_3)_4](BF_4)_2\cdot(CH_3)_2CO$ was dissolved in 20 mL of acetone, and 0.25 g of 1,10-phenanthroline was added to the solution. The yellow solution slowly turned to red. Transformation to the bis(1,10-phenanthroline)palladium(II) complex was completed after 3 h, and the solvent was removed under reduced pressure to give orange solids,

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