

SYNTHESIS AND CHEMISTRY OF THE "METALLOLIGAND" [CpRu(η^2 -dmpm)(η^1 -dmpm)]Cl. X-RAY CRYSTAL STRUCTURES OF [CpRu(η^2 -dmpm)(PPh₃)]Cl AND [CpRu(μ -dmpm)₂Pt(PPh₃)]PF₆ · CH₂Cl₂

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Abstract—CpRuCl(PPh₃)₂ reacts sequentially with bis(dimethylphosphino)methane (dmpm) to yield [CpRu(η^2 -dmpm)(PPh₃)]Cl (1) and then [CpRu(η^2 -dmpm)(η^1 -dmpm)]Cl (2a) from which hexafluorophosphate (2b) and trifluoromethanesulfonate (2c) salts can be obtained by metathesis. Attempts to synthesize CpRu(X)(η^1 -dmpm)₂ were largely unsuccessful and gave predominantly CpRu(X)(η^2 -dmpm) (X = CN (3), C=CPh (4)). In most instances, opening of the chelate ring in 2a did not occur on reaction with coordinatively unsaturated metal complexes and bi- and trimetallic products such as [CpRu(η^2 -dmpm)(μ -dmpm)RuCpCl(PPh₃)]Cl (5), [{CpRu(η^2 -dmpm)(μ -dmpm)}₂ML_n]Cl₂ (ML_n = PdCl₂ (7), PtCl₂ (8)) and [CpRu(η^2 -dmpm)(μ -dmpm)RhCl(CO)(PPh₃)] (CF₃SO₃) (9a) resulted. With Pt(C₂H₄)(PPh₃)₂, however, 2b afforded [CpRu(μ -dmpm)₂Pt(PPh₃)]PF₆ (6). The structures of 1 and 6 were determined by X-ray crystallography. Copyright © 1996 Elsevier Science Ltd

The synthesis and chemistry of heterobimetallic complexes have attracted much interest in recent years, in part because of their potential as models for bifunctional catalysts.¹⁻⁴ Preeminent among the ligands used to stabilize such species against cleavage in subsequent reactions is bis(disphenylphosphino)methane (DPPM) and an increasingly successful route to the directed synthesis of specific heterobimetallic complexes is the use of "metalloligands" containing DPPM.⁵⁻²⁷ A potential drawback of these systems is the considerable bulk of DPPM, particulary when two of these ligands are present in the dimetal complex, and we have consequently been investigating the use of smaller "short-bite" ligands. Despite reports of interesting chemistry of homodinuclear complexes of bis(dimethylphosphine)methane (dmpm),²⁸⁻³⁰ little effort appears to have been made to use this ligand in heterometallic systems. Following our initial report of success in the use of facReBr(CO)₃(η^1 -dmpm)₂ for the synthesis of heterobimetallic complexes,³¹ we have pursued studies of this ligand and report here on further results.

EXPERIMENTAL

All operations were performed under purified nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and were distilled under nitrogen immediately prior to use. Published methods were used to prepare $CpRuX(PPh_{3})_{2}$ (X = Cl,³² CN,³³ C=CPh³⁴), $MCl_2(COD)$ (COD = cycloocta-1,5-diene; M = Pd^{35} , Pt^{36}), $Pt(C_2H_4)(PPh_3)_2^{37}$ and $[RhCl(CO)_2]_2^{38}$ Bis(dimethylphosphino)methane (dmpm) and KPF₆ were purchased from Strem Chemicals. Proton and ${}^{31}P{}^{1}H$ NMR spectra were obtained on an IBM/Bruker AF 200 spectrometer at 200.132 and 81.015 MHz, respectively. Proton and phosphorus chemical shifts are referred to tetramethylsilane (internal) and 85% phosphoric acid (external) respectively with positive shifts downfield of the reference. IR spectra were

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obtained on a Mattson Cygnus 100 Fourier transform instrument. Photochemical reactions were carried out in Pyrex vessels with a Hanovia 450 W high pressure mercury lamp. Microanalyses were by Galbraith Laboratories, Knoxville, TN.

Preparation of $[(\eta^5-C_5H_5)Ru(\eta^2-(CH_3)_2PCH_2P(CH_3)_2)(PC_6H_5)_3)]Cl (1)$

To a solution of 0.458 g (0.630 mmol) of CpRu- $Cl(PPh_3)_2$ in 10 cm³ of toluene was added 0.086 g (0.63 mmol) of dmpm dropwise and the mixture was stirred at 80°C for 8 h. The resulting yellow solid was filtered off, washed with toluene and recrystallized from dichloromethane/hexane (3:1, v:v) to give bright yellow crystals (0.245 g (65%); m.p. 262°C. (dec)). Found: C, 55.8; H, 5.7. Calc. for C₂₈H₃₄P₃ClRu: C, 56.0; H, 5.7%. ¹H NMR (CDCl₃): δ 7.31 (m, 15H, C₆H₅), 4.62 (s, 5H, C_5H_5), 4.22 (m, lH, CH_aH_b), 3.24, (m, lH, $CH_{a}H_{b}$), 1.97 (vt, 6H, CH_{3}), 1.14 (vt, 6H, CH_{3}). ³¹P{¹H} NMR (CDCl₃): δ 56.1 (t, PPh₃), -20.8 $(d, dmpm) (^{2}J(P-P) = 37.5 Hz).^{39}$

Preparation of $[(\eta^5-C_5H_5)Ru(\eta^2-(CH_3)_2PCH_2P(CH_3)_2)$ $(\eta^1-(CH_3)_2PCH_2P(CH_3)_2)]Cl$ (2a)

To a solution of 0.273 g (0.370 mmol) of CpRu $Cl(PPh_3)_2$ in 10 cm³ of toluene was added 0.153 g (1.12 mmol) of dmpm dropwise and the mixture was stirred at 90-100°C for 16 h. The light yellow, microcrystalline solid which formed was filtered off, washed with toluene and dried in vacuo (0.17 g (95%); m.p. 185–187°C.) Found: C, 37.2; H, 7.0 Calc. for C₁₅H₃₃P₄ClRu: C, 38.0; H, 7.0%. ¹H NMR (CDCl₃): δ 4.62 (s, 5H, C₅H₅), 4.20 (m, 2H, CH₂), 3.48 (m, 2H, CH₂), 1.70 (vt, 12H, CH₃), 1.68 (vt, 6H, CH₃), 1.66 (vt, 6H, CH₃). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): $\delta(P_A)$ 16.1 (dt (² $J(P_A - P_B)$) = 39.1; ${}^{2}J(P_{A}-P_{C}) = 43.0$ Hz)), $\delta(P_{B}) - 18.2$ (d $(^{2}J(P_{B}-P_{A}) = 39.1 \text{ Hz})), \delta(P_{C}) - 55.6 \text{ (d})$ $(^{2}J(P_{C}-P_{A}) = 43.0 \text{ Hz}))$. Metathesis of **2a** with KPF₆ in acetone afforded light yellow crystals of the corresponding hexafluorophosphate salt (2b) following filtration through a pad of diatomaceous earth, concentration of the filtrate in vacuo and cooling to 0°C. The trifluoromethanesulfonate salt (2c) was prepared similarly from 2a and silver trifluoromethanesulfonate. Both were identified by their proton and phosphorus NMR spectra which were virtually identical to that for 2a.

Preparation of $(\eta^5$ -C₅H₅)Ru(CN) $(\eta^2$ -(CH₃)₂PCH₂P (CH₃)₂) (**3**)

A solution of $CpRu(CN)(PPh_3)_2$ (0.290 g, 0.400 mmol) and dmpm (0.165 g, 1.2 mmol) in 20 cm³ of

toluene was irradiated for 6 h. Removal of the solvent *in vacuo* gave a yellow, oily residue which was washed with hexane and recrystallized from dichloromethane/hexane (2:1, v:v) at 0°C to give light yellow crystals (0.12 g (91%); m.p. 205°C (dec)). Found: C, 40.1; H, 5.7. Calc. for $C_{11}H_{19}NP_2Ru$: C, 40.2; H, 5.8% IR (Nujol mull): 2361 (m) cm⁻¹ (v_{CN}).⁴⁰ ¹H NMR (CDCl₃): δ 4.70 (s, 5H, C₅H₅), 3.48 (m, 2H, CH₂), 1.73 (t (²J(P—H) = 5.6 Hz), 6H, CH₃), 1.64 (t (²J(P—H) = 5.2 Hz), 6H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ -10.4 (s).

Reaction of CpRu(C=CPh)(PPh₃)₂ with dmpm

A solution of 0.200 g (0.250 mmol) of $CpRu(C = CPh)(PPh_3)_2$ and 0.103 g (0.750 mmol) of dmpm in 25 cm³ of toluene was photolyzed for 6 h. Removal of the solvent in vacuo afforded a pale yellow oil which was washed with hexane. Despite considerable effort, the oil could not be induced to crystallize but its proton and phosphorus NMR spectra showed the presence of only one compound and are consistent with this being CpRu(C= CPh)(η^2 -dmpm) (4). ¹H NMR (CDCl₃): δ 7.8–7.1 $(m, 5H, C_6H_5), 4.72 (s, 5H, C_5H_5), 3.45 (t (^2J(P-H)))$ CH_2), = 10Hz), 2H, 1.69 (m. 12H. CH₃). ³¹P{¹H} NMR (CDCl₃): $\delta - 8.8$ (s).

Preparation of $[(\eta^5-C_5H_5)Ru(\eta^2-(CH_3)_2PCH_2 P(CH_3)_2)(\mu-(CH_3)_2PCH_2P(CH_3)_2)Ru(\eta^5-C_5H_5)(P(C_6H_5)_3)CI]CI \cdot CH_2CI_2$ (5)

A suspension of $CpRuCl(PPh_3)_2$ (0.090 g, 0.12 mmol) and [CpRu(η^2 -dmpm)(η^1 -dmpm)]Cl (0.059 g,0.12 mmol) in 15 cm³ of toluene was refluxed for 4 h during which time a yellow-orange solid separated. This was filtered off, washed with toluene and dried in vacuo (0.136 g (78%); m.p. 118-120°C (dec)). The analytical sample was recrystallized from dichloromethane/acetone/diethyl ether. Found : C, 46.0; H, 5.9. Calc. for C₃₉H₅₅P₅Cl₄Ru₂: C, 45.8; H, 5.4%. ¹H NMR (CDCl₃): δ 7.52–7.30 5.32 $(s, 2H, CH_2Cl_2),$ $(m, 15H, C_6H_5),$ 4.90 $(s, 5H, C_5H_5), 4.26 (s, 5H, C_5H_5), 4.10 (m, 2H, CH_2)$ 2.88 (m, 1H, CH_aH_b), 2.22 (m, 1H, CH_aH_b), 1.89 1.70 $(m, 12H, CH_3),$ $(m, 6H, CH_3),$ 1.20 $(m, 6H, CH_3)$. ³¹P{¹H} NMR (CDCl₃): $\delta(P_A)$ 45.1 $(d(^2J(P_A - P_B) = 45.0))$ 16.8 Hz)), $\delta(\mathbf{P}_{\mathbf{B}})$ $(dd(^{2}J(P_{B}-P_{A}) = 45.0, ^{2}J(P_{B}-P_{C}) = 37.3 \text{ Hz})),$ $\delta(\mathbf{P}_{\rm C})$ 19.8 (q(²J($\mathbf{P}_{\rm C}$ — $\mathbf{P}_{\rm B}$) = ²J($\mathbf{P}_{\rm C}$ — $\mathbf{P}_{\rm D}$) = 37.3 Hz)), $\delta(P_D) - 19.2$, $-19.4 \ (d(^2J(P_D - P_C)) = 37.6$ Hz)).

Preparation of $[(\eta^5-C_5H_5)Ru(\mu-(CH_3)_2PCH_2P(CH_3)_2)_2Pt(P(C_6H_5)_3)]PF_6 \cdot CH_2Cl_2$ (6)

A mixture of 0.063 g (0.13 mmol) of [CpRu(η^2 dmpm)(η^1 -dmpm)]Cl and 0.024 g (0.13 mmol) of KPF_6 in 8 cm³ of acetonitrile was stirred for 1 h. To this was added dropwise a solution of $Pt(C_2H_4)(P(C_6H_5)_3)_2$ in 8 cm³ of dichloromethane. During the course of the addition the color of the solution gradually turned from pale yellow to dark red. After stirring at room temperature for 5 h the solvent was removed in vacuo. The red residue was taken up in 5 cm³ of dichloromethane and filtered through a pad of diatomaceous earth. Dilution with 2 cm³ hexane and concentration under a slow nitrogen purge afforded the product as dark red crystals (0.105 g (78%), m.p. 215°C (dec)). Found : C, 36.1; H, 4.6. Calc. for C₃₄H₅₀F₆P₆Cl₂RuPt: C, 36.3; H, 4.5%. ¹H NMR (CD₂Cl₂): δ 7.68–7.46 (m, 15H, C_6H_5), 4.50 (s, 5H, C_5H_5), 3.25 (m, 4H, CH_2), 1.63 (m, 12H, CH₃). 1.00 (m, 12H, CH₃). ${}^{31}P{}^{1}H{}$ NMR $(CD_2Cl_2): \delta(P_A)$ 11.6 $(dt(J(P_A - P_B) = 29.5,$ $J(P_A - P_C) = 29.6 \text{ Hz}), \delta(P_C) 11.1 (tt(J(P_C - P_A)) =$ 29.6, $J(P_{C}-P_{A}) = 18.5$, ${}^{1}J(Pt-P_{C}) = 1802.2 \text{ Hz})$, $\delta(\mathbf{P}_{\rm B}) - 17.6 \, (\mathrm{dt}(J(\mathbf{P}_{\rm B} - \mathbf{P}_{\rm A}) = 29.5, J(\mathbf{P}_{\rm B} - \mathbf{P}_{\rm C}) = 18.5,$ $^{1}J(\text{Pt}-\text{P}_{\text{B}}) = 3107.6 \text{ Hz})).$

To a solution of $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]Cl$ (0.19 g, 0.40 mmol) in 10 cm³ of dichloromethane was added a dichloromethane solution of 0.057 g (0.20 mmol) of PdCl₂(COD) dropwise with stirring. Slow diffusion of hexane into the resulting yellow– orange solution afforded yellow–orange crystals of the product after 2 d (0.38 g (85%), m.p. 190°C (dec)). Found: C, 29.4; H, 5.6. Calc. for $C_{31}H_{68}Cl_6P_8Ru_2Pd$: C, 29.8; H, 5.7%. ³¹P{¹H} NMR (CD₂Cl₂/C₂H₄Cl₂): $\delta(P_B)$ 17.6 (tt($J(P_B-P_A)$) = 39.3, $J(P_B-P_C)$ = 9.8 Hz)), $\delta(P_C)$ – 3.8 (t($J(P_C-P_B)$) = 9.8 Hz)), $\delta(P_A)$ – 18.1 (d($J(P_A-P_B)$) = 39.3 Hz)).

Preparation of $[{(\eta^5-C_5H_5)Ru(\eta^2-(CH_3)_2PCH_2P(CH_3)_2)(\mu-(CH_3)_2PCH_2P(CH_3)_2)}_2PtCl_2]Cl_2 \cdot 2CH_2 Cl_2 (8)$

This was prepared in analogous fashion to that used for the previous complex and was obtained as greenish-white blocks that became dark green on exposure to moisture (0.22 g (80%), m.p. 197°C (dec)) Found : C, 27.6; H, 5.1 Calc. for $C_{32}H_{70}Cl_8P_8$ $Ru_2Pt: C, 27.7; H, 5.1\%$. ³¹P{¹H} NMR (CD₂Cl₂) : $\delta(P_B)$ 17.4 (tt($J(P_B-P_A) = 38.9, J(P_B-P_C) = 10.9$ Hz)), $\delta(P_{\rm C}) - 8.4$ (t($J(P_{\rm C} - P_{\rm B}) = 10.9$, ${}^{1}J(Pt - P_{\rm C}) = 2382$ Hz)), $\delta(P_{\rm A}) - 18.0$ (d($J(P_{\rm A} - P_{\rm B}) = 38.9$ Hz)).

Reaction of $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)](CF_3SO_3)$ with RhCl(CO)(PPh₃),

To a suspension of $[CpRu(\eta^2-dmpm)(\eta^1$ dmpm)](CF₃SO₃) (0.041 g, 0.087 mmol) in 10 cm³ of toluene was added 0.060 g (0.087 mmol) of $RhCl(CO)(PPh_3)_2$ and the mixture was stirred for 3 h at 90°C. During this time the initial pale yellow solid was replaced by a bright yellow precipitate which was filtered from the cooled reaction mixture, washed with diethyl ether and dried in vacuo. Despite several attempts, an analytically pure sample could not be obtained (the main contaminant appeared from the ³¹P NMR spectrum to be $RhCl(CO)(PPh_3)_2$). However the primary species appears from its ${}^{31}P{}^{1}H$ NMR spectrum to be $[CpRu(\eta^2-dmpm)(\mu-dmpm)RhCl(CO)(PPh_3)](CF_3)$ SO₃) (9a) ${}^{31}P{}^{1}H$ NMR (d₆ acetone): $\delta(P_A)$ 29.8 $(dd({}^{1}J(Rh-P_{A}) = 121.1, {}^{2}J(P_{A}-P_{B}) = 364.9$ Hz)), $\delta(P_B) = -2.8$, $(ddd(^{1}J(Rh-P_B) = 119.4)$, ${}^{2}J(P_{B}-P_{A}) = 364.9, {}^{2}J(P_{B}-P_{C}) = 21.5 \text{ Hz}), \delta(P_{C})$ $(dt(^{2}J(P_{C}-P_{B}) = 21.5, ^{2}J(P_{C}-P_{D}) = 39.4 \text{ Hz})),$ $\delta(P_D) - 16.8, (d(^2J(P_D - P_C) = 39.4 \text{ Hz})).$

X-ray crystallography

General procedures for crystal orientation, unit cell determination and refinement and collection of intensity data have been published.⁴¹ Those specific to the present study are summarized in Table 1. The neutral atom scattering factors used include corrections for the real and imaginary parts of the effects of anomalous dispersion.⁴² All calculations were performed on a VAXstation 3100 computer with the MolEN suite of programs.⁴³

Complex 1. A light-yellow plate crystallized from dichloromethane/hexane was cut to size and mounted on a thin glass fiber with a coat of epoxy cement. The monoclinic cell indicated by the CAD-4 software was confirmed by the observation of 2/mdiffraction symmetry while the systematic absences observed in the final data set (0k0 for k = 2n+1) indicated the space group to be either $P2_1$ or $P2_1/m$. The data was corrected for Lorentz and polarization effects, a linear 1.5% decay in the intensity monitors and for absorption using Ψ scans on several reflections with χ near 90°. The position of the ruthenium atom was provided by direct methods (MULTAN-82⁴⁴) and the intensity statistics obtained in the process indicated the acentric space group $(P2_1)$ to be the correct choice. This was con-

	1	6	
Formula	$C_{28}H_{34}P_3ClRu$	$C_{30}H_{50}P_6F_6Cl_2RuPt$	
fw	600.03	1125.68	
Crystal size (mm)	$0.26 \times 0.33 \times 0.50$	$0.36 \times 0.33 \times 0.43$	
Crystal system	Monoclinic	Orthorhombic	
Space Group	P2,	$P2_{1}2_{1}2_{1}$	
a (Å)	8.5173(6)	11.054(1)	
<i>b</i> (Å)	18.128(2)	18.379(2)	
<i>c</i> (Å)	9.435(1)	21.249(4)	
β (°)	112.332(7)		
$V(Å^3)$	1347.5(5)	4321(2)	
Ζ	2	4	
$\rho_{\rm calc} \ ({\rm g \ cm^{-3}})$	1.48	1.73	
$\mu ({\rm cm}^{-1})$	8.61	40.0	
Range trans factors	0.9635-1.0000	0.7983-0.9973	
Temp (K)	293	293	
Radiation	Mo- K_{α} (Graphite monochromated, $\lambda = 0.71073$ Å)		
Scan type	$\omega/2 heta$	$\omega/2 heta$	
Scan range (°)	$0.80 + 0.2(\tan\theta)$	$0.80 + 0.2(\tan\theta)$	
2θ range (°)	1.0-50.0	1.5-50.0	
Total no. of reflections	2624	4236	
No. unique reflections	2444	4236	
R _{int}	0.027		
No. observed data	$2247(I \ge 2\sigma(I))$	$3101(I \ge 2\sigma(I))$	
No. parameters	297	451	
$(\Delta/\sigma)_{\rm max}$ in last cycle	0.01	0.02	
R"	0.031	0.038	
$R_{\rm w}^{\rm b}$	0.038	0.043	
GOF ^c	1.32	1.26	
$\Delta \rho$ in final ΔF map (e Å ⁻³)	1.04 to -0.19	1.32 to −0.17	

Table 1. Summary of crystallography data

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$

 ${}^{b}R_{w} = [\Sigma w(||F_{o}| - |F_{c}||)^{2} / \Sigma w(|F_{o}|)^{2}]^{1/2} \text{ with } w = 1/(\sigma_{\rm F})^{2}; \sigma_{\rm F} = \sigma(F^{2}) / 2F; \sigma(F^{2}) = [(\sigma_{I})^{2} + (0.04F^{2})^{2}]^{1/2}.$

 ${}^{c}\text{GOF} = [\Sigma w(||F_{o}| - |F_{c}||)^{2}/(N_{o} - N_{c})]^{1/2}$ where N_{o} and N_{c} are, respectively, the number of observations and variables.

firmed by the successful refinement. The structure was developed by successive cycles of full-matrix, least-squares refinement followed by calculation of a $\Delta\rho$ map. In the late stages of the refinement, most hydrogen atoms could be seen in a $\Delta\rho$ map. These were placed in calculated positions (C—H = 0.95 Å) with isotropic displacement parameters 20% larger than those of the attached carbon atoms and updated periodically. At the end of this refinement, the opposite enantiomer was refined and convergence occurred at essentially the same values of R and R_w . With no clear indication of a choice, the initial set of atom coordinates was retained.

Complex 7. A cherry-red crystal, obtained as described in the Experimental section, was cut to give an irregularly-shaped fragment which was mounted on a thin glass fiber with a coat of epoxy cement. The initial cell found by the CAD-4 software appeared to be monoclinic but as *mmm* diffraction symmetry was

observed, an orthorhombic system was indicated. This was confirmed when a new set of reflections with higher and more uniform 2θ values was used to determine the unit cell and the space group was uniquely determined by the systematic absences observed in the final data set. The data were corrected as described for 1, including an anisotropic 8.1% decay in the intensity monitors. The position of the platinum atom was obtained from an origin-removed Patterson function and the remainder of the structure, including the molecule of solvent dichloromethane, was developed and refined as for 1 with an analogous treatment of the hydrogen atoms. Following convergence of the initial model, the opposite enantiomer was refined and found to give significantly lower (> 95% confidence level) values of R and R_w thus indicating the latter to be the correct choice. Final refined atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Synthesis and reactions

The reaction of $CpRuCl(PPh_3)_2$ with one equivalent of dmpm in toluene at 80°C yielded a yellow product which analyzed for $CpRuCl(dmpm)(PPh_3)$



(1). The proton and phosphorus NMR spectra were consistent with the formulation $[CpRu(\eta^2 - dmpm)(PPh_3)]Cl$ and this has been confirmed by an X-ray structure determination. These results contrast with those obtained earlier for the reaction of CpRuCl(PPh_3)₂ with one equivalent of DPPM in aromatic solvents where either CpRuCl(η^2 -DPPM)⁴⁵ or CpRuCl(η^1 -DPPM)(PPh_3)⁴⁶ was formed depending on the concentration of the solution. In those studies, formation of the $[CpRu(\eta^2 - DPPM)(PPh_3)]^+$ cation only occurred in polar solvents.^{45,46} We suggest that the formation of 1 in toluene is at least partly due to the smaller size of the dmpm ligand.

Complex 1 is also formed in substantial amounts when CpRuCl(PPh₃)₂ is reacted with an excess of dmpm under moderate conditions but if higher temperatures and longer reaction times are employed, a light yellow product analyzing for CpRu Cl(dmpm)₂ (2a) is obtained. The ³¹P{¹H} NMR spectrum of 2a is quite consistent with its formulation as [CpRu(η^2 -dmpm)(η^1 -dmpm)]Cl. Thus



three resonances are seen in order of increasing field with relative intensities of 1:2:1. The resonance at $\delta - 55.6$ (P_C) is close to that for free dmpm indicating an uncoordinated phosphorus atom while the one at $\delta - 18.2$ (P_B) with relative intensity 2 is comparable to that for the chelating dmpm ligand in 1. The upfield shift of this resonance relative to that for the coordinated phosphorus atom of the monodentate dmpm (P_A , δ 16.1) is a manifestation of the well-known chelate ring-size effect.⁴⁷ Metathesis of 2a with KPF_6 and with $Ag(CF_3SO_3)$ in acetone afforded, respectively, the corresponding hexafluorophosphate (2b) and trifluoromethanesulfonate (2c) salts which were characterized by their phosphorus NMR spectra. The DPPM analog of 2b has been prepared previously from CpRuCl(PPh₃)₂ and DPPM in methanol in the presence of NH_4PF_6 .⁴⁸ The intermediacy of 1 in the formation of 2a was established by reacting the former with one equivalent of dmpm in toluene at 90°C for 8 h. The product obtained was identical to that prepared as described above. In some preparations of 2a, the phosphorus NMR spectrum showed the presence of a minor product characterized by symmetrical multiplet resonances at δ 23.8 and -18.6 (CD₂Cl₂) in a ratio of 1:2 consistent with the presence of mono- and bidentate dmpm bound to ruthenium. These appeared quite similar to the AA'A"A"'XX' patterns previously observed for fac-M₂(CO)₆(η^2 -L₂)₂(μ -L₂) (M = Mo; $L_2 = MeN(P(OMe)_2)_2 \quad MeN(P(OCH_2CH_2O-))_2.$ M = W; $L_2 = MeN(P(OCH_2CH_2O-))_2)^{49}$ suggesting formulation of the minor product as $[{CpRu(\eta^2-dmpm)}_2(\mu-dmpm)]Cl_2.$

In order to prepare metalloligands which could retain potentially reactive substituents, the reaction of an excess of dmpm with $CpRu(X)(PPh_3)_2$ $(X = CN, C \equiv CPh)$ was studied. In both instances, little or no reaction was observed under thermal conditions but when the reaction mixtures were photolyzed, products characterized as CpRu(X) $(\eta^2$ -dmpm) (X = CN (3), C=CPh (4)) were obtained. Complex 3 was isolated as a crystalline solid which gave satisfactory elemental analyses and its infrared spectrum showed a band attributable to the cyano ligand. The proton and phosphorus NMR spectra indicated the presence of one chelating dmpm ligand and the absence of triphenylphosphine. Complex 4 was obtained as an oil which could not be induced to crystallize. Although no elemental analyses could therefore be



obtained, the proton and phosphorus NMR spectra showed the presence of a single compound and were very similar to those for **3** except for additional

resonances due to the alkynyl ligand indicating 4 to have the same structure as 3. No significant reaction of either 3 or 4 with excess dmpm could be achieved either thermally or photochemically. The difficulty encountered in the synthesis of 3 and 4 and their extreme reluctance to react further with dmpm can be attributed to the coordinatively saturated nature of CpRu(X)(PPh₃)₂ and of CpRu(X)(η^2 -dmpm) (X = CN, C=CPh) and the apparent reluctance of the four-membered Ru(η^2 -dmpm) chelate ring to open (*vide infra*) despite the strain present in it. The more facile substitution reactions when X = Cl can be attributed to the greater ease of loss of chloride which has been well-established.^{45,50,51}

To explore the use of $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]^+$ as a ligand, **2a** was reacted with CpRu Cl(PPh₃)₂. The yellow product obtained analyzed for $[CpRuCl(dmpm)]_2(PPh_3) \cdot CH_2Cl_2$ (5) and on the basis of the proton and phosphorus NMR spectra the structure shown below is proposed. Thus,



four multiplet resonances are observed in the ³¹P{¹H} NMR spectrum which, in order of increasing field, have relative intensities 1:1:1:2. The doublet at δ 45.1 is assigned to triphenylphosphine (P_A) by comparison with the chemical shift observed for this ligand in CpRuCl(PPh₃)₂ (δ 39.1) and in 1 (δ 56.1) and by the fact that it should be coupled only to P_{B} . The same doublet coupling appears in the doublet of doublets centered at δ 16.8 indicating assignment of this resonance to $P_{\rm B}$. By comparison with 2, the resonance at δ 19.8 is assigned to P_c while the highest field resonance belongs to the phosphorus atoms of the chelating dmpm ligand (P_D) . This last resonance appears as a pair of doublets with splittings of 38.4 and 36.8 Hz. This could be the result of the two P_D atoms being diastereotopic because of the chiral nature of the neutral ruthenium center or because of their having slightly different chemical shifts due to a preferred conformation of the $\{CpRuP_AP_B\}$ moiety that places them in slightly different environments. In either event, the average of the couplings seen in the P_D resonances is virtually the same as that between $P_{\rm C}$ and $P_{\rm B}$ leading to the $P_{\rm C}$ resonance appearing as an apparent quartet. The lack of an observable coupling between the two P_D nuclei, despite their apparent non-equivalence can be rationalized if is assumed that the effective P-P

coupling is the sum of components throughout the metal and through the methylene carbon (both twobond couplings) and that these components are of roughly equal magnitude but of opposite sign. Such a situation has been previously described by Grim.⁵²

Based on the ability of *mer*-Mo(CO)₃(η^{2} -L₂)(η^{1} -L₂) (L₂ = MeN(P(OMe)₂)₂,⁴⁹ DPPM⁵⁻⁹) to undergo opening of the four-membered chelate ring in the presence of a coordinatively unsaturated metal center to produce dinuclear complexes, **2b** was reacted with one equivalent of Pt(C₂H₄)(PPh₃)₂. The dark red, crystalline product obtained analyzed for [CpRuPt(dmpm)₂(PPh₃)]PF₆ · CH₂Cl₂ (**6**) and on the basis of its NMR spectra and the results of an X-ray structure determination is formulated as [CpRu(μ -dmpm)₂Pt(PPh₃)]PF₆ · CH₂Cl₂. The



³¹P{¹H} NMR spectrum is readily assigned according to this diagram on the basis of relative peak intensities and the observance of ¹⁹⁵Pt satellites. The resonances for P_A and P_B overlap substantially but the relevant coupling constants could be readily extracted from the ¹⁹⁵Pt satellites associated with the latter. Except for the chemical shift value for the ruthenium-bound phosphorus atoms, the spectrum of **6** is quite similar to that observed for [*fac*-Re(CO)₃(μ -dmpm)₂Pt(PPh₃)]BPh₄³¹ including the magnitudes of the ¹⁹⁵Pt—P coupling constants and the observation of significant coupling between the ruthenium-bound phosphorus atoms and the triphenylphosphine bound to platinum.

 $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]Cl$ Reaction of with $MCl_2(COD)$ (M = Pd, Pt) affords rather insoluble yellow and greenish-white products, respectively, which analyze for MCl₄(CpRu $(dmpm)_2)_2 \cdot nCH_2Cl_2$ (M = Pd, n = 1 (7); M = Pt, n = 2 (8)). While 7 appeared stable to air, 8 soon decomposed to an uncharacterized green solid on exposure. The low solubility of 7 and 8 in deuterated solvents prevented obtaining satisfactory proton spectra however it was possible with some difficulty to obtain their ${}^{31}P{}^{1}H{}$ NMR spectra. Both complexes show multiplet resonances at $ca \delta 17$ and $\delta - 18$ with relative intensities of 1:2 while 7 has a third resonance at $\delta - 3.8$ and 8 has a third at $\delta - 8.4$. This last resonance also possesses ¹⁹⁵Pt satellites thus permitting assignment of the δ 17 and δ –18 resonances, respectively, to monodentate (P_B) and the chelating (P_A) dmpm on ruthenium while the third resonance (P_C) is that for the phosphorus of dmpm bound to palladium or to platinum. The appearance of P_C as a triplet and of P_B as a triplet of triplets can be explained on the



basis of "virtual" coupling and indicates that the ${MCl_2P_2}$ moiety has *trans* geometry. Thus, a large ²J(P-M-P) coupling expected for the trans- P_{C} —M— P_{C} unit results in P_{B} "seeing" two effectively equivalent P_C nuclei in addition to the two equivalent P_A nuclei leading to the observed triplet of triplets appearance. A similar situation has been observed previously for *trans*-RhCl(CO){ $(\mu-\eta^1:\eta^{-2})$ (TPM = tris(diphenylphos- $TPM)Mo(CO)_4$ phino)methane).⁵³ Present also in the spectrum of 7 are weaker resonances at δ 18.0 (dt (J = 26.4, 39.3 Hz)), 3.6 (d (J = 26.4 Hz)) and -17.4(d (J = 39.3 Hz)). These can be assigned, respectively, to P_B , P_C and P_A of the corresponding cis isomer of 7. Despite the satisfactory elemental analysis for 8, its phosphorus NMR spectrum contained a substantial number of minor peaks. We feel this may be due to decomposition (the final NMR solution was distinctly green) during the long time required to obtain the spectrum and consequently it was not possible reliably to determine if any cis-8 were present.

The reaction of $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]Cl$ with $[RhCl(CO)_2]_2$ using a 2:1 Ru:Rh ratio afforded an extremely insoluble yellow solid which could not be adequately characterized. In order to obtain a more tractable product, the reactions of $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]CF_3SO_3$ with RhCl(CO)(PPh₃)₂ in hot toluene and of $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]Cl$ with $[RhCl(CO)_2]_2$ in the presence of one equivalent of triphenylphosphine per rhodium were attempted. In each instance, the yellow, microcrystalline product obtained appeared from its phosphorus NMR spectrum to be a mixture of two species which defied separation and hence satisfactory microanalytical data could not be obtained. The major (and common) product from both reactions showed a ³¹P{¹H} NMR spectrum consisting of four multiplet resonances having relative intensities, in order of increasing field, of 1:1:1:2 suggesting this to be [*trans*-RhCl(CO) (PPh₃)(μ -dmpm)Ru(η^2 -dmpm)Cp]X (X = CF₃SO₃ (9a), Cl (9b)). Thus the resonances at δ 29.8 and -2.8 show doublet splittings typical of ¹J(Rh



(I)-P) couplings and also share a large (364.9 Hz) coupling characteristic of a trans ${}^{2}J(P-P)$ coupling across rhodium(I).41,54 The former has a chemical shift close to that for RhCl(CO) $(PPh_3)_2$ (δ 30.6) and hence can be assigned to triphenylphosphine bound to rhodium (P_A) . The latter is assigned to one end of a bridging dmpm also bound to rhodium (P_B) and the additional doublet splitting seen in it is the ${}^{2}J(P-P)$ coupling between the two ends of this ligand. This same splitting is also seen in the doublet of triplets resonance at δ 17.5 which is in the range found earlier for the bridging dmpm ligand in 2a confirming its assignment to P_c. The highest field resonance is a doublet which occurs at a chemical shift comparable to that found for chelating dmpm bound to ruthenium. The impurity in 9a appeared from the NMR spectrum to be unreacted $RhCl(CO)(PPh_3)_2$ while that in **9b** likely contains monodentate dmpm bound to Rh¹, but even at low temperature it was not possible to find sufficient further resonances to propose a consistent formulation.

In other attempts to prepare heterobimetallic complexes from $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]Cl$, its reactions with $M(CO)_3(CHT)$ and $M(CO)_4$ (NBD) (M = Cr, Mo) were explored. No formation of dinuclear species was observed after extended reaction at room temperature in toluene or tetrahydrofuran solutions based on phosphorus NMR spectra of the solutions which showed unchanged ruthenium complex as the only phosphorus-containing species present. At reflux temperature all systems gave highly insoluble, light brown or green solids which could not be further characterized.

Description of structures

 $[CpRu(\eta^2$ perspective view of the Α $dmpm)(PPh_3)$ ⁺ cation in 1 is given in Fig. 1 while relevant bond distances and interbond angles appear in Table 2. No unusually short interionic contacts are found. The coordination about ruthenium is of the familiar "piano stool" geometry but with a significant distortion because of the short bite of the chelating dmpm and the comparatively large size of the triphenylphosphine ligands. To avoid a close contact between C(23) and the adjacent hydrogen on C(3) (H(3b)) the triphenylphosphine is rotated towards the cyclopentadienyl ring as evidenced by the fact that P(2)-Ru-C' (C' is the centroid of the Cp ring) is significantly smaller than the other two P-Ru-C' angles. This in turn causes a tilt of the cyclopentadienyl ring away from the triphenylphosphine as indicated by the observation that the Ru-C(25) distance is significantly longer than the remaining Ru-C distances. Were this not to occur, the hydrogen on C(25) (H(25)) would make a rather close contact with C(6). All other metrical parameters appear normal.

perspective view of the A $\{CpRu(\mu$ $dmpm)_2Pt(PPh_3)]^+$ cation in 6 is shown in Fig. 2 while pertinent bond distances and interbond angles appear in Table 3. There are no unusual nonbonded contacts. The coordination about ruthenium is virtually the same as was found in 1 while that about platinum is roughly square planar but with a pronounced tetrahedral distortion that is very similar to that observed in $[fac-Re(CO)_3(\mu$ dmpm)₂Pt(PPh₃)]Br · H₂O.³¹ The Pt-Ru distance of 2.769(1) Å is clearly consistent with the presence of a Pt-Ru single bond and compares favorably with similar ones in $[Ru_2Pt(CO)_7(\mu-PPh_2)(\mu-H)]$ (Pcy_3)] (2.7248(5) Å),⁵⁵ $[Ru_3Pt(CO)(\mu-CO)_2(\mu-CO)_2)$ PPh_2)(μ -H)(Pcy_3)] (2.764(2) Å),⁵⁵ [$Ru_4Pt(CO)_{13}(\mu$ -H)(COD)] (2.6837(8)–2.872(1) Å), 56 [Ru₃Pt(CO)₁₀ $(\mu-H)_2(COD)$] (2.718(1)-2.7942(9) Å)⁵⁶ and $[Ru_3Pt(CO)_7(\mu-PPh_2)(\mu_4-\eta^2-C \equiv CBu^t)(DPPE)]$ (2.770(1), 2.729(1) Å).⁵⁷ All other aspects of the structure appear normal.



Fig. 1. Perspective view of the $[CpRu(\eta^2-dmpm)(PPh_3)]^+$ cation in 1. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.



Fig. 2. Perspective view of the $[CpRu(\mu-dmpm)_2 Pt(PPh_3)]^+$ cation in 6. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbons which are arbitrarily small for clarity. Hydrogen atoms are omitted.

Ru - P(1)	2.289(1)	Ru-C(25)	2.257(6)
Ru - P(2)	2.314(2)	Ru—C(26)	2.223(7)
Ru - P(3)	2.290(2)	Ru—C(27)	2.200(7)
RuC(24)	2.220(6)	Ru—C(28)	2.211(7)
P(1) - Ru - P(2)	97.34(7)	$P(1)$ — Ru — C'^a	128.6(2)
P(1) - Ru - P(3)	70.56(5)	$P(2)$ — Ru — C'^a	120.7(2)
P(2)— Eu — $P(3)$	99.34(5)	$P(3)$ — Ru — C'^a	127.6(2)

Table 2. Selected bond lengths (Å) and interbond angles (°) for $[CpRu(\eta^2-dmpm)(PPh_3)]Cl(1)$

"C' is the centroid of the Cp ring.

PtRu	2.769(1)	RuC(29)	2.23(2)
Pt - P(1)	2.315(3)	Ru—C(30)	2.20(2)
PtP(4)	2.267(4)	Ru—C(31)	2.20(2)
PtP(5)	2.324(4)	Ru—C(32)	2.19(2)
Ru - P(2)	2.240(4)	Ru—C(33)	2.21(2)
Ru—P(3)	2.248(4)		
Ru - Pt - P(1)	86.4(1)	Pt-Ru-P(2)	83.3(1)
Ru - Pt - P(4)	83.1(1)	Pt - Ru - P(3)	96.6(1)
Ru - Pt - P(5)	166.78(9)	Pt-Ru-C'a	120.4(6)
P(1) - Pt - P(4)	161.8(2)	P(2) - Ru - P(3)	93.6(2)
P(1) - Pt - P(5)	95.0(1)	$P(2)$ - Ru - C'^a	126.6(7)
P(4) - Pt - P(5)	98.6(1)	P(3)RuC' ^a	125.6(7)

Table 3. Selected bond lengths (Å) and interbond angles (°) for $[CpRu(\mu-dmpm)_2Pt(PPh_3)]PF_6 \cdot CH_2Cl_2$ (6)

"C' is the centroid of the Cp ring.

CONCLUSION

The metalloligand $[CpRu(\eta^2-dmpm)(\eta^1-dmpm)]^+$ has proven to be moderately successful in the synthesis of heterobimetallic complexes. Unfortunately, in only one instance was opening of the chelate dmpm ligand observed to give a metalmetal bonded product. This contrasts with the behavior of previously studied $[M(\eta^2-DPPM)(\eta^1-DPPM)]$ moieties and can presumably be traced to the smaller size and greater basicity of dmpm which should render it more tightly bound to ruthenium.

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