

can be attributed in part to the electron-withdrawing character of the  $\text{CH}_2\text{NH}_3^+$  group. The seemingly anomalous Cr-Cr bond length in the recently reported tetranuclear  $\text{Cr}_4(\text{O}_2\text{CCH}_3)_4(\text{OCH}_2\text{CH}_2\text{NMe}_2)_4$  compound<sup>41</sup> can be explained by the absence of two of the bridging acetate groups in each of the two dinuclear units. The influence of the axial ligands on the Cr-Cr bond length cannot be dismissed, but the effects of the halide ligands in **1** and **2** are unknown since these are the first structurally characterized  $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$  compounds found with other than nitrogen or oxygen axial donor atoms.

The dinuclear structures found for **1** and **2** afford a partial explanation of the magnetic properties reported by Herzog and Kalies for **1**.<sup>18</sup> Thus, the depressed magnetic moment in **1** of  $0.79 \mu_{\text{B}}/\text{Cr}$  most likely results from a combination of superexchange interactions across the  $[\text{Cr}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4]^{4+}$  unit combined with some direct exchange propagated by means of the Cr-Cr bond. Since previous work has suggested the presence of some  $\text{Cr}^{3+}$  impurities in  $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$  compounds,<sup>43</sup> a more detailed study using variable-temperature magnetic susceptibility measurements is needed to unravel antiferromagnetic and paramagnetic impurity contributions

in  $\text{Cr}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4\text{Br}_4 \cdot 4\text{H}_2\text{O}$ . The solution magnetic moment observed for **1** of  $4.83 \mu_{\text{B}}$  is close to the spin-only value of  $4.90 \mu_{\text{B}}$  for four unpaired electrons in high-spin  $\text{Cr}^{2+}$ . This suggests that the dinuclear units do not remain intact in solution. Support for this suggestion is derived from a recent structure containing mononuclear square-planar  $\text{Cr}^{2+}$  ions coordinated by monodentate trifluoroacetate ligands.<sup>44</sup> This tendency toward facile Cr-Cr bond scission in solution is in marked contrast to analogous  $\text{Mo}_2^{4+}$  complexes where simple substitution reactions leave the  $\text{Mo}^4\text{-Mo}$  bond intact.

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**Registry No.** **1**, 92126-99-3; **2**, 92127-00-9; Cr, 7440-47-3.

**Supplementary Material Available:** Tables IIA and IIIA (anisotropic thermal parameters for  $\text{Cr}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4\text{Br}_4 \cdot 4\text{H}_2\text{O}$  (**1**) and  $\text{Cr}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4\text{Cl}_4 \cdot 3\text{H}_2\text{O}$  (**2**), respectively), Tables IVA and VA (hydrogen-bonded contacts in **1** and **2**, respectively), listings of observed and calculated structure factor amplitudes for **1** and **2**, and figures of unit cell contents for **1** and **2** (23 pages). Ordering information is given on any current masthead page.

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### 3,3',4,4'-Tetramethyl-1,1'-diphosphaferrocene (DPF): Template Ligand for the Formation of Polymetallic Complexes

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The donor properties of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene (DPF) were investigated by preparing a series of 13 complexes of this ligand. Reaction of DPF with  $(\text{THF})\text{M}(\text{CO})_5$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) gives the monometallic monoligand complexes  $(\text{DPF})\text{M}(\text{CO})_5$ , from which the bimetallic biligand  $(\text{DPF})[\text{M}(\text{CO})_5]_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and  $\text{M}(\text{CO})_5(\text{DPF})\text{M}'(\text{CO})_5$  ( $\text{M} = \text{Cr}, \text{M}' = \text{Mo}, \text{W}; \text{M} = \text{Mo}, \text{M}' = \text{W}$ ) were prepared. Similarly, DPF and  $\text{Mn}_2(\text{CO})_{10}$  produce  $(\text{DPF})\text{Mn}_2(\text{CO})_9$  and  $(\text{DPF})[\text{Mn}_2(\text{CO})_9]_2$ . Reaction of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  with DPF in refluxing methanol produces *trans*- $(\text{DPF})_4\text{RuCl}_2$  while reaction of  $(\text{PPh}_3)_3\text{RuCl}_2$  with DPF produces the bimetallic biligand  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$  containing both bridging and terminal chlorides. These complexes have been characterized by elemental analyses, infrared,  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, and mass spectrometry. The ligand DPF is shown to be a better donor than  $\text{PPh}_3$  toward ruthenium(II) by chemical reactivity studies. Cotton-Kraihanzel force constants for the  $(\text{DPF})\text{M}(\text{CO})_5$  complexes suggest that DPF is a better  $\sigma$  donor and much better  $\pi$  acceptor than 1-phenyl-3,4-dimethylphosphole. The crystal structure of  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$  has been determined by three-dimensional X-ray diffraction techniques. The molecule crystallizes in the triclinic space group  $P\bar{1}$  in a unit cell of dimensions  $a = 12.566$  (4) Å,  $b = 13.100$  (4) Å,  $c = 12.202$  (4) Å,  $\alpha = 110.58$  (2)°,  $\beta = 104.24$  (2)°,  $\gamma = 66.08$  (2)°, and  $\rho_{\text{calcd}} = 1.62 \text{ g cm}^{-3}$  with  $Z = 1$ . Refinement converged to  $R = 0.069$  with 3814 independent reflections. The structure indicates that the phospholyl rings remain fully aromatic in the complex. The three C-C bond lengths are almost equal, with a mean value of 1.415 (4) Å. The two ruthenium centers are six-coordinate with asymmetric chloride bridges, terminal chlorides, terminal  $\text{PPh}_3$ , and two bridging DPF ligands. The DPF phosphorus atoms are eclipsed in contrast to free DPF where phosphorus eclipses the  $\beta$ -carbon. The Ru-P(DPF) distances are short (2.2935 (4) Å, average), which is shorter than the Ru-P( $\text{PPh}_3$ ) distances (2.311 (4) Å). The two triphenylphosphines occupy anti positions (one on each ruthenium) such that the two sides of the phospholyl rings are not in equivalent environments. This inequivalence is manifested in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of this compound.

#### Introduction

Polymetallic complexes are receiving considerable attention for several reasons.<sup>2</sup> Paramount among these is the notion that metals held proximate may exhibit cooperativity in both their chemical and physical properties. This notion portends

useful applications for polymetallic complexes in such areas as catalysis,<sup>3</sup> conducting materials,<sup>2</sup> and enzyme models.<sup>4</sup> Most of the polymetallic complexes synthesized to date contain metal-metal bonds<sup>5</sup> or bridging ligands such as halides,

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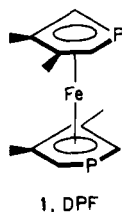
Table I. Elemental Analysis for the Complexes of DPF

complex	% C		% H		% P		% Fe		% metal	
	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
(DPF)W(CO) <sub>5</sub>	33.89	34.12	2.66	2.52	10.30	10.57	9.30	9.11	30.56	31.00
(DPF)[W(CO) <sub>5</sub> ] <sub>2</sub>	28.51	28.30	1.73	1.89	6.70	7.01	6.05	5.98	39.76	40.02
(DPF)Mo(CO) <sub>5</sub>	39.69	40.39	3.11	3.16	12.06	12.13	10.89	10.65	18.68	18.22
(DPF)[Mo(CO) <sub>5</sub> ] <sub>2</sub>	35.20	35.45	2.13	2.07	8.27	8.43	7.47	7.31	25.60	25.46
(DPF)Cr(CO) <sub>5</sub>	43.40	43.74	3.40	3.37	13.19	13.19	11.91	11.85	11.06	10.66
(DPF)[Cr(CO) <sub>5</sub> ] <sub>2</sub>	39.88	39.94	2.42	2.34	9.36	8.60	8.46	8.22	15.71	14.78
(OC) <sub>5</sub> Mo(DPF)Cr(CO) <sub>5</sub>	37.39	38.02	2.27	2.20	8.78	8.53	7.93	7.51	13.60	13.06 Mo
(OC) <sub>5</sub> Mo(DPF)W(CO) <sub>5</sub>	31.50	32.98	1.91	2.04	7.40	7.05	6.68	6.45	21.96	22.77 W
									11.46	10.65 Mo
									23.17	23.26 W
(OC) <sub>5</sub> Cr(DPF)W(CO) <sub>5</sub>	33.25	33.63	2.01	1.98	7.81	7.88	7.05	7.03	6.55	5.85 Cr
(DPF)Mn <sub>2</sub> (CO) <sub>9</sub>	39.37	38.93	2.50	2.54	9.69	9.68	<i>a</i>		17.19	16.55
(DPF)[Mn <sub>2</sub> (CO) <sub>9</sub> ] <sub>2</sub>	35.93	36.76	1.60	1.83	6.19	6.31	<i>a</i>		21.96	20.88
(DPF) <sub>4</sub> RuCl <sub>2</sub>	44.91	44.87	4.99	4.83	19.30	19.05	17.40	17.06	5.52 <sup>b</sup>	5.41
[(PPh <sub>3</sub> )Ru(DPF)Cl <sub>2</sub> ] <sub>2</sub>	50.60	50.04	4.35	4.35	13.05	12.59	7.84	7.62	9.96 <sup>b</sup>	9.18

<sup>a</sup> Manganese interferes with the iron analysis. <sup>b</sup> Chloride analysis.

pseudohalides, carbon monoxide, or bis(phosphines).<sup>6</sup> In general, these systems do not lend themselves to the facile synthesis of mixed-metal complexes containing two or more different metals.

Fewer polymetallic complexes contain ligands that are themselves metal complexes, though several complexes of functionalized ferrocenes have been prepared.<sup>7</sup> Some of these complexes have been shown to be good asymmetric hydrogenation catalysts. In the functionalized ferrocenes, the iron atom is isolated from the donor site(s) and displays no cooperativity with the other metal center(s). In contrast, 1,1'-diphosphaferrocenes such as DPF (**1**) contain an iron atom



1, DPF

directly bound to the phosphorus donor site, which is contained in a heterocyclic aromatic ring.<sup>8-10</sup> The phosphorus atoms of DPF are strong electron attractors<sup>9b,c</sup> and are thus especially adapted to  $\pi$  acceptance.<sup>11</sup>

Free DPF exists in an eclipsed configuration,<sup>9</sup> wherein the phosphorus atoms eclipse the  $\beta$ -carbons of the other ring. From theoretical studies,<sup>12</sup> the barrier to rotation of the phospholyl ring seems low, and despite the aromaticity of the phospholyl ring, crystallographic studies<sup>8</sup> indicate that ring puckering is also a low-energy process. With these ideas in

Table II. Carbonyl Stretching Frequencies and Force Constants for LM(CO)<sub>5</sub> Complexes

complex	$\nu_{\text{CO}}$ , <sup>a</sup> cm <sup>-1</sup>	$k_1$ , <sup>b</sup>	$k_2$ , <sup>b</sup>	$k_3$ , <sup>b</sup>
(DPF)Cr(CO) <sub>5</sub>	2066 (A <sub>1</sub> )	15.59	16.01	0.31
	1991 (B <sub>1</sub> )			
	1952 (E)			
(DPF)Mo(CO) <sub>5</sub> <sup>c</sup>	1952 (A <sub>1</sub> )	15.87	16.09	0.31
	2074 (A <sub>1</sub> )			
	1996 (B <sub>1</sub> )			
	1957 (E)			
(DPF)W(CO) <sub>5</sub>	1957 (A <sub>1</sub> )	15.62	15.96	0.25
	2072 (A <sub>1</sub> )			
	1988 (B <sub>1</sub> )			
	1956 (E)			
(DMPP)Cr(CO) <sub>5</sub>	1956 (A <sub>1</sub> )	15.33	15.83	0.27
	2060 (A <sub>1</sub> )			
	1980 (B <sub>1</sub> )			
	1946 (E)			
(DMPP)Mo(CO) <sub>5</sub> <sup>d</sup>	1938 (A <sub>1</sub> )	15.62	16.01	0.29
	2072 (A <sub>1</sub> )			
	1991 (B <sub>1</sub> )			
	1954 (E)			
(DMPP)W(CO) <sub>5</sub>	1954 (A <sub>1</sub> )	15.35	15.67	0.22
	2067 (A <sub>1</sub> )			
	1970 (B <sub>1</sub> )			
	1942 (E)			
	1942 (A <sub>1</sub> )			

<sup>a</sup> All spectra measured in decaline solution. <sup>b</sup> Units of mdyn/Å calculated according to ref 15. <sup>c</sup> Graham bonding parameters:<sup>16</sup>  $\Delta\sigma = -0.27$ ,  $\Delta\pi = 0.52$ . <sup>d</sup> Graham bonding parameters:<sup>16</sup>  $\Delta\sigma = -0.18$ ,  $\Delta\pi = 0.35$ .

mind we have commenced an investigation of the donor properties of DPF and report herein complexes with some representative metal carbonyls and ruthenium.

## Results and Discussion

Reaction of DPF with (THF)M(CO)<sub>5</sub> cleanly produces the monometallic monoligate complexes (DPF)M(CO)<sub>5</sub> (M = Cr, Mo, W) rather than polymers<sup>13</sup> as evidenced by elemental analyses (Table I) and their mass spectra, which in each case shows a parent ion whose mass is consistent with the complex being monomeric. Numerous LM(CO)<sub>5</sub> complexes have previously been prepared,<sup>14</sup> and several different spectroscopic techniques have been utilized to evaluate the nature and strength of the metal-ligand bond in these complexes. These techniques include C-O stretching frequencies and force constants<sup>15</sup> and their analysis to obtain  $\sigma$ - and  $\pi$ -bonding ligand

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Table III.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR Data for  $\text{C}_6\text{D}_6$  Solutions of the DPF Complexes<sup>a</sup>

complex	$\delta(\text{CH}_3)$	$\delta(\text{H})$	$^2J_{\text{PH}}$ , Hz	$\delta(^{31}\text{P})$	$J_{\text{PP}}$ , Hz	$\Delta\delta(^{31}\text{P}) = \delta(\text{complex}) - \delta(\text{ligand})$
DPF	2.11	3.74	36.1	-72.0		
(DPF)W(CO) <sub>5</sub>	1.52, 1.64	3.09, 3.67	33.4, 36.1	-47.60, -66.54	5.1 <sup>b</sup>	24.4, 5.46
(DPF)[W(CO) <sub>5</sub> ] <sub>2</sub>	1.47	3.42	33.9	-46.25	<i>c</i>	25.75
(DPF)Mo(CO) <sub>5</sub>	1.56, 1.65	3.15, 3.67	34.4, 36.1	-23.49, -67.17	5	48.51, 4.83
(DPF)[Mo(CO) <sub>5</sub> ] <sub>2</sub>	1.49	3.47	34.4	-22.02	5	50
(DPF)Cr(CO) <sub>5</sub>	1.52, 1.62	3.13, 3.74	33.2, 36.1	11.69, -67.71	5	83.69, 4.29
(DPF)[Cr(CO) <sub>5</sub> ] <sub>2</sub>	1.46	3.54	34.4	13.57		85.57
(OC) <sub>5</sub> Cr(DPF)Mo(CO) <sub>5</sub>	1.44, 1.46	3.47, 3.54	33.7, 34.4	13.65 Cr -21.95 Mo	5	85.65 Cr 50.05 Mo
(OC) <sub>5</sub> W(DPF)Cr(CO) <sub>5</sub>	1.45	3.48	33.2	14.17 Cr -46.79 W	5 <sup>d</sup>	86.17 Cr 25.21 W
(OC) <sub>5</sub> W(DPF)Mo(CO) <sub>5</sub>	1.47, 1.48	3.42, 3.47	32.4, 36.1	-21.20 Mo -46.56 W	5 <sup>e</sup>	50.8 Mo 25.44 W
(DPF)Mn <sub>2</sub> (CO) <sub>9</sub>	1.49, 1.56	3.47, 3.77	33.4, 34.4	22 br -66.95		94 5.05
(DPF)[Mn <sub>2</sub> (CO) <sub>9</sub> ] <sub>2</sub>	2.09	4.23	33.2	29 v br		1.06
(DPF) <sub>4</sub> RuCl <sub>2</sub>	2.07, 1.94	3.75, 4.02	35.6, "14.2"	12.29 -72.87	0	84.29 -0.87
[(PPh <sub>3</sub> )Ru(DPF)Cl <sub>2</sub> ] <sub>2</sub>	1.98, 1.84	2.93, 4.2	"13.7", "13.7"	55.76 (PPh <sub>3</sub> ) 17.73 (DPF)	41.7	61.76 (PPh <sub>3</sub> ) 89.73 (DPF)

<sup>a</sup> In CDCl<sub>3</sub> solution. <sup>b</sup>  $^1J_{\text{WP}} = 257$  Hz. <sup>c</sup>  $^1J_{\text{WP}} = 251$  Hz. <sup>d</sup>  $^1J_{\text{WP}} = 259$  Hz. <sup>e</sup>  $^1J_{\text{WP}} = 259$  Hz. Typical values of  $^1J_{\text{WP}}$  for (R<sub>3</sub>P)W(CO)<sub>5</sub> complexes are 235–280 Hz: Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573.

Table IV.  $^{13}\text{C}\{^1\text{H}\}$  NMR Data for Complexes of DPF in CDCl<sub>3</sub> Solution

complex	$\delta(^{13}\text{C})$ ( $J_{\text{PC}}$ , Hz)						
	C <sub>α</sub>		C <sub>β</sub>		CO		
	complexed	free	complexed	free	cis	trans	
DPF		82.1 (61.6)		97.5 (7.5)			16.1
(DPF)W(CO) <sub>5</sub>	73.4	84.0 (61.0)	95.7	99.2 (7.3)	194.7 (8.5)	198.1 (30.8)	14.4, 14.7
(DPF)Mo(CO) <sub>5</sub>	74.5 (4.9)	83.8 (61.0)	95.8	99.0 (7.3)	204.2 (12.2)	208.6 (31.7)	14.5, 14.7
(DPF)Cr(CO) <sub>5</sub>	73.3 (3.7)	83.7 (61.0)	95.6	99.2 (7.3)	215.3 (17.1)	NO <sup>a</sup>	14.3, 14.5
(DPF)[W(CO) <sub>5</sub> ] <sub>2</sub>	77.5	...	96.6	...	194.3 (8.5)	197.1 (31.7)	14.7, 14.9
(DPF)[Mo(CO) <sub>5</sub> ] <sub>2</sub>	78.2	...	96.5	...	203.8 (11.0)	208.6 (30)	14.7, 14.9
(DPF)[Cr(CO) <sub>5</sub> ] <sub>2</sub> <sup>b</sup>	78.0 (4.9)	...	98.8	...	NO	NO	14.6, 14.9
(OC) <sub>5</sub> W(DPF)Cr(CO) <sub>5</sub> <sup>b</sup>	78.1 (4.9) Cr	...	96.6 (W)	...	198.3 (8.5) W	...	...
	78.0 (0) W	...	96.4 (Cr)	...	214.9 (17.1) Cr	NO	14.7, 14.9
(CO) <sub>5</sub> W(DPF)Mo(CO) <sub>5</sub> <sup>b</sup>	78.0 (7.3) Mo	...	97.1 (Mo)	...	194.3 (8.5) W	...	...
	77.85 (0) W	...	96.8 (W)	...	203.8 (11.0) Mo	NO	14.7, 14.9
(OC) <sub>5</sub> Mo(DPF)Cr(CO) <sub>5</sub>	79.0 (6.9) Mo	...	97.1 (Mo)	...	203.8 (11.0) Mo	...	...
	78.0 (4.9) Cr	...	96.6 (Cr)	...	214.9 (17.1) Cr	NO	14.7, 14.9
[(PPh <sub>3</sub> )Ru(DPF)(μ-Cl)Cl <sub>2</sub> ] <sub>2</sub> <sup>c</sup>	68.13, 67.9	...	94.2, 93.8	...	...	...	13.5, 13.7

<sup>a</sup> NO = not observed. <sup>b</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>c</sup> PPh resonances,  $\delta$  ( $J_{\text{PC}}$ , Hz): C<sub>1</sub>, 135.1 (56.8); C<sub>2,6</sub>, 134.6 (8.5); C<sub>3,5</sub>, 127.3 (9.7); C<sub>4</sub>, 129.1 (0).

parameters,<sup>16</sup>  $\delta(^{13}\text{C}(\text{CO}))$ ,<sup>17</sup>  $\delta(^{31}\text{P})$  for phosphorus donor complexes,<sup>18</sup> and interrelationships among these parameters.<sup>18</sup> Investigation of these spectroscopic data reveals the following with regard to the donor properties of the ligand DPF. In concert with the a priori expectation that DPF would possess significant  $\pi$  acceptor properties, the Graham treatment of the Cotton-Kraihanzel force constants (Table II) suggests that DPF has good  $\pi$  accepting capability ( $\Delta\pi = 0.52$ ). This may be compared with the  $\pi$  accepting capability of 1-phenyl-3,4-dimethylphosphole (DMPP),  $\Delta\pi = 0.35$ , which is on this basis a poorer  $\pi$  acceptor<sup>19</sup> than DPF. Also, the  $\sigma$  donor ability of DPF ( $\Delta\sigma = -0.27$ ) appears to be somewhat greater than that of DMPP ( $\Delta\sigma = -0.18$ ) on the basis of force constants. However, it should be noted that this treatment has been criticized, and both its validity and reliability have been discussed.<sup>20</sup>

In contrast, the  $^{31}\text{P}$  coordination chemical shift (Table III) for DPF in the (DPF)M(CO)<sub>5</sub> complexes is large (83.69,

48.51, and 24.4 ppm for M = Cr, Mo, and W, respectively) compared<sup>21</sup> to 51.3, 29.7, and 10 ppm for (DMPP)M(CO)<sub>5</sub> (M = Cr, Mo, and W, respectively). Hence, on the basis of the phosphorus coordination chemical shifts, DPF appears to be a better  $\sigma$  donor toward these three metals than DMPP.

In addition, the  $\delta(^{13}\text{C}(\text{CO}))$  chemical shifts (Table IV) of these complexes are in the normal ranges,<sup>17</sup> and they correlate linearly with the CO force constants and the  $^{31}\text{P}$  chemical shifts in precisely the same way as Bodner<sup>18</sup> has found for several phosphorus donor ligands. On the basis of the positions of the DPF data on Bodner's correlations, it appears that DPF has similar donor properties to P(OCH<sub>3</sub>)<sub>3</sub> and we shall see that crystallographic data suggest a rather strong DPF-ruthenium bond (vide infra).

The (DPF)M(CO)<sub>5</sub> complexes cleanly react with (THF)-M'(CO)<sub>5</sub>, where M' is the same or a different metal, to produce the bimetallic biligate complexes (OC)<sub>5</sub>M(DPF)M'(CO)<sub>5</sub>. The facile syntheses of these bimetallic complexes of DPF afford an excellent opportunity to gain information regarding cooperativity in polymetallic complexes. The  $\nu_{\text{CO}}$  values for these complexes (Table V) indicate that each

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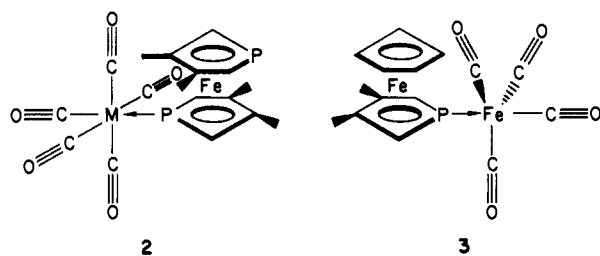
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Table V. Infrared Data in the CO Region for Polymetallic Complexes of DPF in Decalin Solution

complex	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$
(DPF)[Cr(CO) <sub>5</sub> ] <sub>2</sub>	2070, 1960, 1950, 1940
(DPF)[Mo(CO) <sub>5</sub> ] <sub>2</sub>	2075, 1960, 1950, 1940
(DPF)[W(CO) <sub>5</sub> ] <sub>2</sub>	2075, 1955, 1945, 1935
(OC) <sub>5</sub> Cr(DPF)W(CO) <sub>5</sub>	2075, 2065, 1955, 1950, 1940
(OC) <sub>5</sub> Cr(DPF)Mo(CO) <sub>5</sub>	2075, 2065, 1960, 1950, 1940
(OC) <sub>5</sub> Mo(DPF)W(CO) <sub>5</sub>	2070, 2065, 1960, 1955, 1940
(DPF)Mn <sub>2</sub> (CO) <sub>9</sub>	2080, 2010, 1990, 1970, 1945
(DMPP)Mn <sub>2</sub> (CO) <sub>9</sub> <sup>a</sup>	2084, 2010, 1993, 1972, 1939
(DPF)[Mn <sub>2</sub> (CO) <sub>9</sub> ] <sub>2</sub>	2085, 2015, 1990, 1975, 1940, 1925

<sup>a</sup> DMPP = 1-phenyl-3,4-dimethylphosphole; data from: Mathey, F. *J. Organomet. Chem.* **1975**, *93*, 377.

M(CO)<sub>5</sub> moiety is essentially independent of the others, as separate vibrations are observed for each at energies very similar to those observed for the (DPF)M(CO)<sub>5</sub> complexes (Table II). Similar conclusions are reached from the <sup>1</sup>H NMR and <sup>31</sup>P NMR data (Table III). Coordination of DPF to an M(CO)<sub>5</sub> group gives rise to an upfield shift of both  $\delta(\text{CH}_3)$  and  $\delta(\text{ring H})$  along with a small decrease in <sup>2</sup>J<sub>PH</sub> for the ring hydrogens. Normally, one would anticipate a downfield movement of these resonances upon coordination, as electron density is removed from DPF. An upfield shift indicates that the coordinated phosphorus is less involved in removing electron density from the ring than the free phosphorus or that metal electron density is placed back onto the ring by  $\pi$  back-donation. Both of these effects are probably in part responsible for the upfield shift of the coordinated ring resonances. The resonances for the methyl groups of the uncoordinated ring also move to higher field upon coordination, but the chemical shift of the ring protons of the uncoordinated ring are essentially unaffected by coordination. These observations suggest that these complexes probably possess structure 2, in which the metal M and the ring phosphorus



lie nearly in the plane of the phosphole ring, similar to what was observed<sup>9</sup> for 3, placing the methyl groups of the uncoordinated ring in the shielding region of the anisotropic carbonyls. This geometry places the free phosphorus atom in an optimum orientation to coordinate to a second metal center. For the (DPF)[M(CO)<sub>5</sub>]<sub>2</sub> complexes, a further upfield shift of the methyl resonances is observed, consistent with the above interpretation, and the ring protons resonate at a value intermediate between those observed for the free and coordinated ring of the (DPF)M(CO)<sub>5</sub> complexes.

The proton and phosphorus chemical shifts of the (OC)<sub>5</sub>M(DPF)M'(CO)<sub>5</sub> complexes are nearly the same as those observed for the coordinated ring in the respective (DPF)M(CO)<sub>5</sub> complexes, suggesting that the metal centers are essentially chemically independent. Electrochemical studies of these complexes also indicate approximate redox independence of the metal centers.<sup>22</sup> For each complex that possesses anisochronous phosphorus nuclei, a small J<sub>PP</sub> was observed (J<sub>PP</sub> ~ 5 Hz). By comparison, for monosubstituted<sup>9</sup> DPF molecules J<sub>PP</sub> = 10 ± 2 Hz.

The <sup>13</sup>C resonances of the coordinated phospholyl ring (Table IV) behave in a parallel fashion to the proton resonances and support the interpretations offered above.

In order to ascertain whether DPF could span a metal-metal bond, this ligand was reacted with Co<sub>2</sub>(CO)<sub>8</sub> and Mn<sub>2</sub>(CO)<sub>10</sub>. No complexes could be isolated from the Co<sub>2</sub>(CO)<sub>8</sub> reactions under a variety of conditions. We only observed decomposition of Co<sub>2</sub>(CO)<sub>8</sub>. However, with Mn<sub>2</sub>(CO)<sub>10</sub>, in the presence of Me<sub>3</sub>NO,<sup>23</sup> both (DPF)Mn<sub>2</sub>(CO)<sub>9</sub> and (DPF)[Mn<sub>2</sub>(CO)<sub>9</sub>]<sub>2</sub> were formed under mild conditions. The infrared data for these complexes in the CO region (Table V) indicate that the DPF is bound to the axial position collinear with the Mn-Mn bond. The infrared data for (DPF)Mn<sub>2</sub>(CO)<sub>9</sub> are nearly identical with that observed<sup>24</sup> for (DMPP)Mn<sub>2</sub>(CO)<sub>9</sub>, suggesting similar Mn-P bond strengths toward Mn(0) for DPF and DMPP. Aside from being tri- and pentametallic complexes, these complexes are otherwise unexceptional. Thermolysis, in the absence and presence of Me<sub>3</sub>NO, as well as photolysis of these complexes did not affect conversion to (DPF)Mn<sub>2</sub>(CO)<sub>8</sub> or (DPF)<sub>2</sub>Mn<sub>2</sub>(CO)<sub>6</sub>.<sup>25</sup> This is probably because the P-P distance in DPF is considerably greater than the Mn-Mn distance in complexes of this type (vide infra).

Ruthenium complexes of DPF turned out to be more interesting. Reaction of DPF with RuCl<sub>3</sub>·3H<sub>2</sub>O in refluxing methanol produced *trans*-(DPF)<sub>4</sub>RuCl<sub>2</sub> in good yield. This is similar to the reaction<sup>26</sup> of RuCl<sub>3</sub>·2H<sub>2</sub>O with PPh<sub>3</sub> where (PPh<sub>3</sub>)<sub>4</sub>RuCl<sub>2</sub> is formed but not with<sup>27</sup> DMPP. However, both DPF and DMPP react with (PPh<sub>3</sub>)<sub>3</sub>RuCl<sub>2</sub> to form (DPF)<sub>4</sub>RuCl<sub>2</sub> and (DMPP)<sub>4</sub>RuCl<sub>2</sub>, respectively, if an excess of the ligand is employed. The complex *trans*-(DPF)<sub>4</sub>RuCl<sub>2</sub> shows two <sup>31</sup>P resonances, one at essentially the same chemical shift as observed for free DPF ( $\delta(^{31}\text{P}) = -72.87$  and  $-72.0$ , respectively) and one at  $\delta$  12.29, which is 84.29 ppm downfield of free DPF at room temperature. These resonances appear as sharp singlets with 1:1 relative intensity. This complex is not very soluble, and hence even in dilute solution *trans*-(DPF)<sub>4</sub>RuCl<sub>2</sub> is substitutionally much more inert<sup>28</sup> than either (PPh<sub>3</sub>)<sub>4</sub>RuCl<sub>2</sub> or (PPh<sub>3</sub>)<sub>3</sub>RuCl<sub>2</sub>, both of which readily dissociate PPh<sub>3</sub> in solution. (DMPP)<sub>4</sub>RuCl<sub>2</sub> is similarly substitutionally inert.<sup>27</sup> Thus, toward ruthenium(II) DMPP and DPF appear to have similar donor strengths. The <sup>1</sup>H NMR spectrum of *trans*-(DPF)<sub>4</sub>RuCl<sub>2</sub> displays two methyl resonances ( $\delta$  2.07 and 1.94), the former very near the free ligand methyl resonance ( $\delta$  2.11) and the latter slightly upfield. Two ring proton resonances are also observed (Figure 1): a doublet at  $\delta$  3.75 (<sup>2</sup>J<sub>PH</sub> = 35.6 Hz) compared to the free ligand ( $\delta$  3.74, <sup>2</sup>J<sub>PH</sub> = 36.1 Hz) and a five-line [AX<sub>2</sub>]<sub>4</sub> multiplet at  $\delta$  4.02. The simplicity of the <sup>1</sup>H and <sup>31</sup>P NMR spectra along with the observation of a single  $\nu_{\text{RuCl}}$  at 312.5 cm<sup>-1</sup> establishes<sup>27</sup> the *trans* geometry for (DPF)<sub>4</sub>RuCl<sub>2</sub>.

If (Ph<sub>3</sub>P)<sub>3</sub>RuCl<sub>2</sub> and DPF are reacted in a 1:1 molar ratio, a red complex analyzing (Table I) for (PPh<sub>3</sub>)Ru(DPF)Cl<sub>2</sub> is formed. The <sup>31</sup>P NMR spectrum of this complex consists of a triplet at  $\delta$  55.76 and a doublet at  $\delta$  17.73 (<sup>2</sup>J<sub>PP</sub> = 41.7 Hz). Hence, there are three phosphorus atoms coordinated to ruthenium, and this is only consistent with a dimeric structure: [(PPh<sub>3</sub>)Ru(DPF)( $\mu$ -Cl)Cl]<sub>2</sub>. The <sup>1</sup>H NMR spectrum (Table III; Figure 1) shows that both the methyl and ring phospholyl protons are anisochronous. The ring protons give rise to two apparent 1:2:1 triplets at  $\delta$  4.2 and 2.93. These triplets arise

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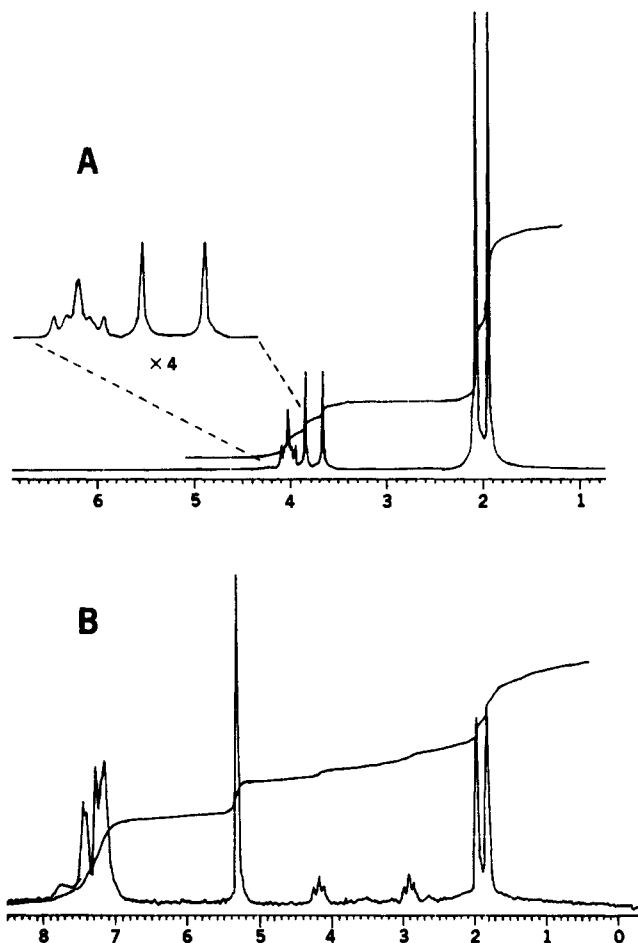
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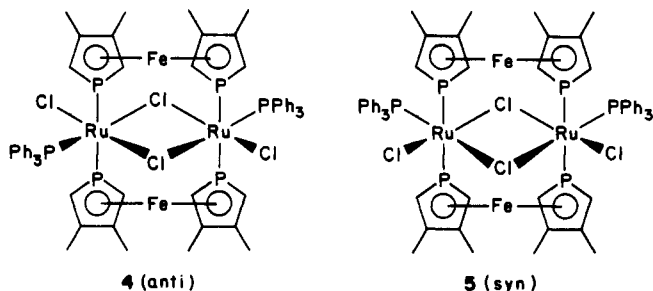
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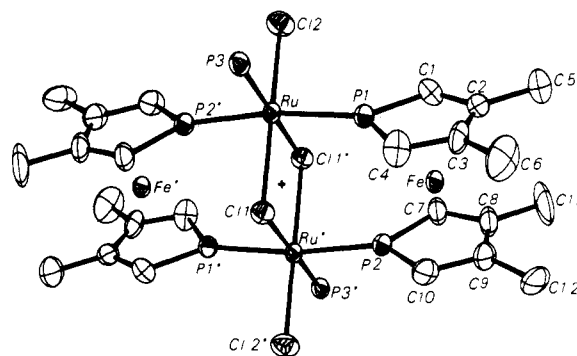


**Figure 1.** 200-MHz  $^1\text{H}$  NMR spectra (in  $\text{CDCl}_3$  at 300 K): (A) *trans*-(DPF) $_4$ RuCl $_2$ ; (B)  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$ . For (B) the  $\text{CH}_2\text{Cl}_2$  solvate is evident at  $\delta$  5.30.

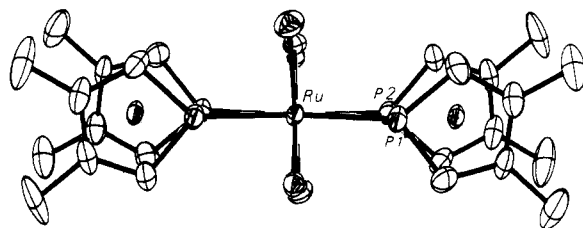
from  $[\text{AX}_2]_2$  spin systems where A represents phospholyl phosphorus nuclei and X represents the ring protons. The fact that these resonances are simple triplets indicates that there is no coupling of the ring protons to the  $\text{PPh}_3$  phosphorus nuclei. An alternative analysis that the two triplets arise from coupling to the  $\text{PPh}_3$  phosphorus was eliminated by studying the field dependence of the  $^1\text{H}$  NMR at 80, 100, and 200 MHz, which clearly demonstrated that the ring proton triplets and the two methyl resonances represent chemical shift inequivalent nuclei. The resonance at  $\delta$  4.2 comes at essentially the same chemical shift as observed for the coordinated phospholyl ring protons in *trans*-(DPF) $_4$ RuCl $_2$ , but the triplet at  $\delta$  2.93 is considerably upfield of this. These NMR results are consistent with two structures (4 and 5).



For both the anti (4) and syn (5) structures, the two sides of the phospholyl rings are not related by any symmetry element and, as a result, would give rise to two chemical shifts for each type of nucleus. Those groups that are proximate to the  $\text{PPh}_3$  moieties should experience shielding due to the anisotropy of the phenyl rings. Inequivalence is also observed



**Figure 2.** ORTEP plot of the structure of  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$  showing the atom-labeling scheme (50% probability ellipsoids). Phenyl groups have been omitted for clarity.



**Figure 3.** View of the  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$  molecule along the Ru-Ru' vector. Phenyl groups have been omitted for clarity.

in the  $^{13}\text{C}\{^1\text{H}\}$  NMR of this complex.

In order to establish the exact molecular structure of this complex and gain further information regarding the bonding therein, an X-ray crystal structure was obtained. An ORTEP drawing of the complex is shown in Figure 2, and Figure 3 shows the molecule as viewed along the Ru-Ru' axis. The fractional atomic coordinates are given in Table VI, and important bond distances and angles are given in Table VII. The molecule possesses a center of symmetry (structure 4) and lies on a crystallographic inversion center. There are several features of this structure that are of interest. The phospholyl rings appear to retain their aromaticity<sup>9</sup> when coordinated, as the three C=C bond lengths are essentially equal with a mean value of 1.415 (4) Å, which compares with a mean value of 1.410 (2) Å in free<sup>9</sup> DPF. The two phospholyl rings of each DPF are not strictly planar but slightly bent around the axes defined by C1 and C4 and C7 and C10, respectively. The carbon moieties of each ring are both planar (Table VIII) within experimental error, but the phosphorus atoms lie out of these mean planes by 0.068 (2) and 0.131 (2) Å away from the iron to which they are bound, with an average displacement of 0.0995 (2) Å. This compares to similar values for DPF (average displacement 0.04 (1) Å). The dihedral angle between mean planes C1 to C4 and C1-P1-C4 is 3.1° and between C7 to C10 and C7-P2-C10 is 5.8°, indicating that one phospholyl ring is bent more than the other. In DPF itself, phosphorus eclipses the  $\beta$ -carbon of the other ring; but as is evident in Figure 3, phosphorus eclipses phosphorus in  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$ .

The phosphorus-carbon bond distances are equivalent, with a mean value of 1.744 (6) Å compared to a mean value of 1.767 (1.7) Å in DPF itself and a C-P-C angle of 91.0 (3)° compared to 88.22 (8)° in free DPF. Hence, upon coordination, the P-C bonds shorten slightly, and the CPC bond angle increases slightly. These changes indicate that both phospholyl rotation and ring puckering are relatively low-energy processes and small deviations can occur with little influence on the aromaticity of the phospholyl ring.

The ruthenium-phosphorus distances suggest that DPF forms a stronger bond to ruthenium ( $d(\text{RuP}) = 2.294$  (1) Å) than does triphenylphosphine ( $d(\text{RuP}) = 2.311$  (1) Å). This

Table VI. Table of Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
Ru	0.43738 (4)	0.09579 (4)	0.13790 (4)	1.79 (1)	CIS11	0.899 (2)	0.160 (2)	0.054 (2)	9.7 (4)*
Cl1	0.5768 (1)	0.0918 (1)	0.0223 (2)	2.35 (4)	CIS12	1.016 (2)	0.013 (2)	0.185 (2)	10.3 (5)*
Cl2	0.3039 (2)	0.0721 (2)	0.2312 (2)	3.31 (5)	CIS13	0.965 (2)	0.237 (2)	0.290 (2)	12.7 (6)*
Fe	0.25444 (9)	0.19560 (9)	-0.1668 (1)	2.17 (3)	CIS21	0.8677 (7)	0.0725 (7)	0.0813 (8)	13.0 (2)*
P1	0.2957 (2)	0.2110 (2)	0.0273 (2)	2.33 (4)	CIS22	0.9526 (6)	0.2489 (6)	0.1523 (6)	11.4 (2)*
C1	0.1512 (7)	0.2312 (7)	-0.0401 (8)	3.3 (2)	CIS23	0.971 (1)	0.150 (1)	0.323 (1)	17.5 (4)*
C2	0.1056 (7)	0.3216 (7)	-0.0952 (7)	3.4 (2)	HC1	0.1081	0.1862	-0.0396	7*
C3	0.1903 (7)	0.3734 (6)	-0.0817 (7)	3.1 (2)	HC4	0.3656	0.3396	-0.0103	7*
C4	0.2983 (8)	0.3193 (6)	-0.0223 (8)	3.5 (2)	H1C5	-0.0584	0.3124	-0.1534	7*
C5	-0.0195 (9)	0.360 (1)	-0.1559 (9)	5.4 (3)	H2C5	-0.0601	0.4391	-0.1164	7*
C6	0.165 (1)	0.4743 (8)	-0.129 (1)	5.9 (3)	H3C5	-0.0177	0.3534	-0.2356	7*
P2	0.4050 (2)	0.0278 (2)	-0.2260 (2)	2.26 (4)	H1C6	0.2326	0.4953	-0.1108	7*
C7	0.2621 (7)	0.0310 (7)	-0.2737 (7)	3.2 (2)	H2C6	0.1450	0.4510	-0.2121	7*
C8	0.1967 (7)	0.1161 (7)	-0.3360 (7)	3.5 (2)	H3C6	0.1014	0.5387	-0.0938	7*
C9	0.2621 (8)	0.1774 (7)	-0.3420 (7)	3.8 (2)	HC7	0.2310	-0.0179	-0.2600	7*
C10	0.3785 (7)	0.1448 (6)	-0.2790 (7)	3.1 (2)	HC10	0.4330	0.1818	-0.2678	7*
C11	0.0726 (9)	0.132 (1)	-0.399 (1)	6.3 (4)	H1C11	0.0434	0.0828	-0.3841	7*
C12	0.220 (1)	0.2672 (9)	-0.4088 (8)	6.4 (3)	H2C11	0.0235	0.2112	-0.3710	7*
P3	0.4486 (2)	0.2571 (1)	0.2884 (2)	2.14 (4)	H3C11	0.0738	0.1135	-0.4815	7*
C13	0.5567 (6)	0.2252 (6)	0.4156 (6)	2.5 (2)	H1C12	0.2793	0.2972	-0.4000	7*
C14	0.6548 (7)	0.2580 (8)	0.4516 (8)	3.9 (2)	H2C12	0.2007	0.2318	-0.4900	7*
C15	0.7361 (9)	0.222 (1)	0.5466 (9)	5.2 (3)	H3C12	0.1517	0.3287	-0.3784	7*
C16	0.7205 (9)	0.154 (1)	0.5993 (8)	5.0 (3)	HC14	0.6672	0.2085	0.4136	7*
C17	0.625 (1)	0.1241 (9)	0.5650 (8)	5.3 (3)	HC15	0.8023	0.2461	0.5736	7*
C18	0.5379 (7)	0.1587 (7)	0.4710 (7)	3.2 (2)	HC16	0.7774	0.1273	0.6600	7*
C19	0.3185 (6)	0.3572 (6)	0.3664 (7)	2.5 (2)	HC17	0.6144	0.0785	0.6042	7*
C20	0.2059 (7)	0.3622 (7)	0.3110 (7)	3.2 (2)	HC18	0.4704	0.1369	0.4478	7*
C21	0.1112 (6)	0.4432 (7)	0.3677 (7)	3.4 (2)	HC20	0.1949	0.3105	0.2354	7*
C22	0.1240 (7)	0.5227 (7)	0.4757 (8)	3.6 (2)	HC21	0.0346	0.4445	0.3316	7*
C23	0.2369 (7)	0.5128 (7)	0.5319 (8)	3.5 (2)	HC22	0.0573	0.5823	0.5105	7*
C24	0.3317 (7)	0.4328 (7)	0.4755 (7)	3.0 (2)	HC23	0.2480	0.5615	0.6092	7*
C25	0.4823 (6)	0.3602 (6)	0.2460 (7)	2.7 (2)	HC24	0.4084	0.4295	0.5128	7*
C26	0.5877 (7)	0.3222 (6)	0.1909 (7)	3.2 (2)	HC26	0.6432	0.2462	0.1951	7*
C27	0.6099 (8)	0.3990 (7)	0.1572 (9)	4.5 (2)	HC27	0.6813	0.3739	0.1256	7*
C28	0.5311 (9)	0.5076 (8)	0.1618 (9)	5.0 (3)	HC28	0.5471	0.5580	0.1332	7*
C29	0.4280 (9)	0.5447 (7)	0.2071 (8)	4.8 (2)	HC29	0.3726	0.6204	0.2095	7*
C30	0.4037 (8)	0.4706 (7)	0.2501 (8)	3.9 (2)	HC30	0.3325	0.4973	0.2822	7*

<sup>a</sup> Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + (ab \cos \gamma)B(1,2) + (ac \cos \beta)B(1,3) + (bc \cos \alpha)B(2,3)]$ .

latter value should be compared with those found<sup>29</sup> for  $(\text{PPh}_3)_3\text{RuCl}_2$  ( $d(\text{RuP}) = 2.374$  (6), 2.412 (6), 2.230 (8) Å). Also by way of comparison, the RuP distances<sup>27</sup> for  $(\text{DMPP})_3\text{Ru}(\text{CO})\text{Cl}_2$  are 2.365 (1), 2.356 (1), and 2.411 (1) Å. All these data suggest that the ruthenium-DPF bond in  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$  is short and strong.

The chloride bridging is asymmetric, with the Ru-Cl bond trans to  $\text{PPh}_3$  ( $d(\text{RuCl}) = 2.496$  (1) Å) being longer than that trans to the terminal chloride ( $d(\text{RuCl}) = 2.421$  (1) Å), and both of these are longer than the terminal ruthenium chloride bond ( $d(\text{RuCl}) = 2.409$  (1) Å). Previously reported values<sup>30</sup> for ruthenium chloride bond lengths fall in the range  $d(\text{RuCl}) = 2.387\text{--}2.55$  Å. Thus, both the ruthenium-phosphorus and ruthenium-chloride bond lengths are found in their normal ranges.

The Ru-Ru distance (3.683 (1) Å) and P-P distance (3.376 (2) Å) explain why we were unsuccessful in preparing a manganese carbonyl complex of DPF wherein DPF spans the Mn-Mn bond, as  $d(\text{MnMn})$  is much shorter than these values, being<sup>31</sup> 2.9038 Å in  $\text{Mn}_2(\text{CO})_{10}$  and 2.9032 Å in  $(\text{Et}_3\text{P})_2\text{Mn}_2(\text{CO})_8$ .

Because of the novel nature of the two ruthenium complexes reported herein, we tested them as catalysts<sup>32</sup> for the homogeneous hydrogenation of 1-hexene at ambient temperature

and pressure. Whereas  $(\text{PPh}_3)_3\text{RuCl}_2$  serves to catalyze this hydrogenation under these conditions, the two DPF complexes of ruthenium do not. This is probably a consequence of the lack of facile ligand exchange<sup>27</sup> in the DPF complexes.

The mass spectra of the DPF complexes (Table IX) display some interesting regularities. The spectrum of each complex studied displays a weak-intensity molecular ion. The intensity of the molecular ion decreases in the order  $\text{W} > \text{Cr} > \text{Mo} > \text{Mn}$ , suggesting that the complexes have this order of thermal stabilities. The metal-DPF ion is also prominent in each spectrum. Whereas this ion is the most intense ion in the spectra of the  $(\text{DMPP})\text{M}(\text{CO})_5$ , the most intense ion in the spectra of the  $(\text{DPF})\text{M}(\text{CO})_5$  complexes is due to the ligand DPF. Hence, the decomposition modes of the two complexes are different. This is also reflected in differences in the chemistry of the two series of complexes. For DMPP the *cis*-bis-ligand complexes are easily prepared,<sup>21</sup> and these complexes undergo a novel photochemical Diels-Alder dimerization of the coordinated phospholes.<sup>21</sup> In contrast, we were uniformly unsuccessful in preparing bis-ligand metal carbonyl complexes with the DPF ligand. These data suggest that the DMPP metal-ligand bond is stronger than the DPF metal-ligand bond in the metal carbonyls, and this is consistent with the comparative  $\sigma$ -bonding parameters for the two ligands (Table II).

## Conclusion

The data reported herein demonstrate that DPF behaves as a normal phosphorus donor ligand toward representative metal carbonyls and ruthenium(II) with donor properties similar to phosphites. Despite the presence of two phosphorus donor centers in the ligand DPF, sequential coordination of

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Table VII. Selected Bond Lengths (Å) and Angles (deg) for  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2^a$ 

Ru-Ru'	3.683 (1)	P1-C1	1.753 (6)	} 1.744 (3)
Ru-Cl1	2.421 (1)	P1-C4	1.741 (6)	
Ru-Cl1'	2.496 (1)	P2-C7	1.734 (6)	
Ru-Cl2	2.409 (1)	P2-C10	1.748 (6)	} 1.417 (4)
Ru-P1	2.311 (1)	C1-C2	1.415 (9)	
Ru-P2'	2.297 (1)	C2-C3	1.429 (9)	
Ru-P3	2.290 (1)	C3-C4	1.402 (8)	} 1.518 (5)
Fe-P1	2.250 (2)	C7-C8	1.428 (9)	
Fe-P2	2.262 (2)	C8-C9	1.390 (9)	
Fe-C1	2.069 (6)	C9-C10	1.443 (9)	} 2.072 (2)
Fe-C2	2.068 (5)	C2-C5	1.524 (9)	
Fe-C3	2.083 (6)	C3-C6	1.513 (9)	
Fe-C4	2.068 (6)	C8-C11	1.525 (9)	} 91.0 (3)
Fe-C7	2.067 (6)	C9-C12	1.512 (9)	
Fe-C8	2.059 (6)			
Fe-C9	2.088 (6)			} 112.0 (2)
Fe-C10	2.077 (6)			
Cl1-Ru-Cl1'	83.02 (4)	C1-P1-C4	90.4 (3)	} 91.0 (3)
Cl1-Ru-Cl2	169.21 (5)	C7-P2-C10	91.7 (3)	
Cl1-Ru-P3	98.46 (5)	P1-C1-C2	112.8 (5)	} 112.0 (2)
Cl1'-Ru-Cl2	86.63 (5)	P1-C4-C3	112.7 (5)	
Cl1'-Ru-P3	178.38 (4)	P2-C7-C8	111.9 (5)	
Cl2-Ru-P3	91.85 (5)	P2-C10-C9	110.6 (4)	} 112.2 (2)
Ru-Cl1-Ru'	96.98 (4)	C1-C2-C3	111.0 (5)	
P1-Ru-Cl1	86.51 (5)	C2-C3-C4	112.7 (5)	
P1-Ru-Cl1'	89.68 (5)	C7-C8-C9	112.5 (5)	} 112.8 (5)
P1-Ru-Cl2	96.48 (5)	C8-C9-C10	112.8 (5)	
P1-Ru-P3	91.07 (5)			
P1-Ru-P2'	172.52 (5)			} 92.71 (5)
P2-Ru'-Cl1	86.73 (5)			
P2-Ru'-Cl1'	85.43 (5)			
P2-Ru'-Cl2	90.97 (5)			} 92.71 (5)
P2-Ru'-P3	92.71 (5)			

<sup>a</sup> Mean value P-C phenyl rings, 1.841 (3). Mean value C-C phenyl rings, 1.385 (2)

Table VIII

Equations of Least-Squares Planes for  $[(\text{PPh}_3)\text{Ru}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$ 

plane	dist. <sup>a</sup> Å		equation <sup>b</sup>	
PL1	C1*	-0.014 (9)	0.2727x - 0.4198y - 0.8657z - 0.0749	
	C2*	0.014 (8)		
	C3*	-0.005 (8)	0.2799x - 0.4670y - 0.8388z + 0.0654	
	C4*	0.011 (9)		
	C5*	0.006 (11)		
	C6*	-0.016 (12)		
PL2	P1'	-0.068 (2)	0.2811x - 0.4819y - 0.8299z - 3.1322	
	Fe	1.636 (1)		
	PL3	P1*	0.000 (2)	0.2426x - 0.4044y - 0.8818z - 3.2529
		C1*	0.000 (9)	
		C4*	0.000 (9)	
		C7*	0.024 (8)	
PL4	C8*	-0.032 (9)	0.2426x - 0.4044y - 0.8818z - 3.2529	
	C9*	-0.011 (9)		
	C10*	-0.005 (8)		
	C11*	0.005 (12)		
	C12*	0.031 (10)		
	P2	0.131 (2)		
	Fe	-1.629 (1)		
	P2	0.000 (2)		
	C7	0.000 (8)		
	C10	0.000 (8)		
Dihedral Angles, deg				
PL1/PL2	3.1	PL1/PL3	4.1	
PL3/PL4	5.8			

<sup>a</sup> Starred atoms were used for computing mean planes. <sup>b</sup> Orthogonalized coordinates according to: Blow, D. M. *Acta Crystallogr.* 1960, 13, 168.

each is readily achieved rather than forming polymers. Even though the phosphorus donor centers in DPF are directly bonded to two metal centers in its complexes, very little cooperativity is observed in any of the physical or chemical

Table IX. Mass Spectral Data for Some DPF and DMPP Complexes

complex	m/e, <sup>a</sup> %
(DPF)Cr(CO) <sub>5</sub>	470 (6, M), 442 (2, M - CO), 414 (1, M - 2CO), 386 (6, M - 3CO), 358 (72, M - 4CO), 330 (52, Cr(DPF)), 278 (100, DPF)
(DMPP)Cr(CO) <sub>5</sub> <sup>b</sup>	380 (10, M), 240 (100, Cr(DMPP))
(DPF)Mo(CO) <sub>5</sub>	516 (2, M), 376 (12, Mo(DPF)), 278 (100, DPF)
(DMPP)Mo(CO) <sub>5</sub> <sup>b</sup>	426 (21, M), 286 (100, Mo(DMPP))
(DPF)W(CO) <sub>5</sub>	602 (10, M), 574 (1, M - CO), 546 (2, M - 2CO), 518 (4, M - 3CO), 490 (4, M - 4CO), 462 (44, W(DPF)), 278 (100, DPF)
(DMPP)W(CO) <sub>5</sub> <sup>b</sup>	512 (40, M), 372 (100, W(DMPP))
(DPF)[Cr(CO) <sub>5</sub> ] <sub>2</sub>	622 (1, M), 330 (20, Cr(DPF)), 278 (100, DPF)
(DPF)[Mo(CO) <sub>5</sub> ] <sub>2</sub>	754 (2, M), 376 (6, Mo(DPF)), 278 (100, DPF)
(DPF)[W(CO) <sub>5</sub> ] <sub>2</sub>	926 (6, M), 462 (50, W(DPF)), 278 (100, DPF)
Mo(CO) <sub>5</sub> (DPF)Cr(CO) <sub>5</sub>	708 (0.5, M), 470 (6, (DPF)Cr(CO) <sub>5</sub> ), 330 (54, Cr(DPF)), 278 (100, DPF)
W(CO) <sub>5</sub> (DPF)Cr(CO) <sub>5</sub>	794 (9, M), 602 (22, (DPF)W(CO) <sub>5</sub> ), 470 (18, (DPF)Cr(CO) <sub>5</sub> ), 278 (100, DPF)
(DPF)Mn <sub>2</sub> (CO) <sub>9</sub>	666 (0.5, M), 333 (8, Mn(DPF)), 278 (100, DPF)

<sup>a</sup> For the most abundant isotopes <sup>52</sup>Cr, <sup>98</sup>Mo, <sup>184</sup>W. <sup>b</sup> Data from ref 21 at 70 eV.

properties of the DPF complexes. The complex  $[(\text{PPh}_3)\text{R}(\text{DPF})(\mu\text{-Cl})\text{Cl}]_2$  is the first complex of this type reported for ruthenium, and further studies of its reaction chemistry are in progress.

### Experimental Section

(A) **General Procedures.** NMR spectra (chemical shifts ( $\delta$ ) from internal Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C and from external 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P;  $\delta$  positive for downfield shifts in all cases) were recorded on Bruker WP-80 and Wp-200 and JEOL FX-100 spectrometers in the FT mode. Mass spectra were recorded on a MS 30 AEI spectrometer at 70 eV. Elemental analyses were performed by Service Central D'Analyse de CNRS. Infrared spectra were recorded on Perkin-Elmer 499 and 599 instruments and a Polytec far-IR 30 FT interferometer. All reactions and manipulations were performed under an argon atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone ketyl. Chromatographic separations were performed on silica gel columns (70-230 mesh Merck). Irradiation was performed with a medium-pressure mercury lamp (Hanovia) in quartz photochemical apparatus. DPF was prepared according to the literature<sup>9</sup> and purified by column chromatography on silica gel with eluant benzene-hexane (10:90). Metal carbonyls were commercial reagents (Alfa) and were used as received.

(B) **Syntheses. (DPF)M(CO)<sub>5</sub> (M = Cr, Mo, W) Complexes.** These three complexes were synthesized by the same general method. A solution containing 2 mmol of the appropriate M(CO)<sub>6</sub> in 200 mL of dry THF was irradiated for 1 h in a quartz reactor under argon at room temperature. Then, 2 mmol of purified DPF was added, and the resultant solutions were stirred magnetically under argon at room temperature for 2 h (M = Cr), 4 h (M = Mo), and 5 h at reflux (M = W). The THF was then removed under vacuum and the residue chromatographed on silica gel under argon with hexane-benzene (90:10). In this way the (DPF)M(CO)<sub>5</sub> complexes were isolated as red crystalline solids in ~60% yield along with an approximately 20% yield of (DPF)[M(CO)<sub>5</sub>]<sub>2</sub>. The (DPF)M(CO)<sub>5</sub> complexes have the greater R<sub>f</sub> values. Elemental analyses are given in Table I.

(DPF)[M(CO)<sub>5</sub>]<sub>2</sub> (M = Cr, Mo, W) **Complexes.** In the same manner, 2 mmol of M(CO)<sub>6</sub> and 1 mmol of DPF prepared 50-60% yields of (DPF)[M(CO)<sub>5</sub>]<sub>2</sub> as red crystalline solids. Elemental analyses are given in Table I.

(OC)<sub>5</sub>M(DPF)M'(CO)<sub>5</sub> (M = Cr, M' = Mo, W; M = Mo, M' = W) **Complexes.** A solution containing 1 mmol of M'(CO)<sub>6</sub> in 200 mL of dry THF was irradiated for 1 h in a quartz reactor under argon at room temperature. Then, 1 mmol of (DPF)M(CO)<sub>5</sub> prepared above



was added, and the resultant solution was stirred magnetically for 5 h at room temperature under argon. After the solvent was removed under vacuum and the residue was chromatographed on silica gel under argon with hexane–benzene (80:20), the mixed-metal complexes were obtained as red crystalline solids in 55–60% yields. Elemental analyses are given in Table I.

**(DPF)Mn<sub>2</sub>(CO)<sub>9</sub>.** A solution containing 2 mmol of DPF, 2 mmol of Mn<sub>2</sub>(CO)<sub>10</sub>, and 4.4 mmol of dry Me<sub>3</sub>NO in 100 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was stirred magnetically under argon at room temperature for 30 min. The CH<sub>2</sub>Cl<sub>2</sub> was removed under vacuum, and the residue was chromatographed on silica gel under argon with hexane–benzene (90:10) to produce the title compound as a red crystalline solid in 70% yield.

**(DPF)[Mn<sub>2</sub>(CO)<sub>9</sub>]<sub>2</sub>.** In the same way, reaction of 1 mmol of DPF with 2 mmol of Mn<sub>2</sub>(CO)<sub>10</sub> and 4.4 mmol of Me<sub>3</sub>NO in CH<sub>2</sub>Cl<sub>2</sub> afforded the title compound as a red crystalline solid in 50% yield.

**trans-Ru(DPF)<sub>4</sub>Cl<sub>2</sub>.** A solution containing 1 g (3.82 mmol) of RuCl<sub>3</sub>·3H<sub>2</sub>O in 50 mL of dry methanol was refluxed under nitrogen for 1 h and then cooled to room temperature. To this solution was added, under nitrogen, a solution containing 5.56 g (20 mmol) of DPF in 50 mL of dry toluene. The resultant deep red solution was stirred magnetically under nitrogen at room temperature overnight. Then, 100 mL of solvent was removed under vacuum and the resultant solution left standing under nitrogen at room temperature for 2 days to form large red-orange crystals. These were separated by filtration under nitrogen, washed with hexane (3 × 25 mL), and vacuum dried to afford 2.92 g (59.6%) of red-orange crystals, mp 248–252 °C. IR:  $\nu_{\text{RuCl}}$  (polythene) 312.5,  $\nu_{\text{RuP}}$  377.0,  $\nu_{\text{C=C}}$  (KBr) 1450, 1420 cm<sup>-1</sup>.

**[(PPh<sub>3</sub>)Ru(DPF)( $\mu$ -Cl)Cl]<sub>2</sub>.** A solution containing 6.38 g (6.66 mmol) of freshly prepared<sup>26</sup> (Ph<sub>3</sub>P)<sub>3</sub>RuCl<sub>2</sub> and 1.956 g (7.0 mmol) of DPF in 100 mL of toluene was refluxed under nitrogen for 2 h. After cooling to room temperature, the solution had become deep brown and contained orange microcrystals. These were separated by filtration under nitrogen, washed with hexane and diethyl ether, and vacuum dried to produce 5.60 g (~100%) of orange microcrystals, mp 278 °C. Recrystallization from chloroform–ether under nitrogen produced red-orange crystals suitable for x-ray analysis; mp 278 °C. This compound forms solvates very readily. IR:  $\nu_{\text{RuCl}}$  (polythene) 281, 305, 323,  $\nu_{\text{RuP}}$  374,  $\nu_{\text{C=C}}$  (KBr) 1483, 1435 cm<sup>-1</sup>.

**(C) X-ray Data Collection and Processing.** A dark red 0.106 × 0.25 × 0.30 mm parallelepiped of [(PPh<sub>3</sub>)Ru(DPF)( $\mu$ -Cl)Cl]<sub>2</sub> was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Phillips PW1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation. A systematic search in reciprocal space showed that the crystals belong to the triclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) by using 25 carefully selected reflections and the standard Phillips software. Final results: C<sub>60</sub>H<sub>62</sub>P<sub>6</sub>Cl<sub>4</sub>Fe<sub>2</sub>Ru<sub>2</sub>·2CHCl<sub>3</sub>, mol wt 1663.4,  $a$  = 12.566 (4) Å,  $b$  = 13.100 (4) Å,  $c$  = 12.202 (4) Å,  $\alpha$  = 110.58 (2)°,  $\beta$  = 104.24 (2)°,  $\gamma$  = 66.08 (2)°,  $V$  = 1706 Å<sup>3</sup>,  $Z$  = 1,  $\rho_{\text{calcd}}$  = 1.62 g cm<sup>-3</sup>,  $\mu$  = 123.40 cm<sup>-1</sup>,  $F_{000}$  = 836, space group  $P\bar{1}$ .

The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2 $\sigma$  level. The total scan width in the  $\theta$ – $2\theta$  flying step scan used as  $\Delta\theta$  = 0.9 + (Cu K $\alpha_1$  K $\alpha_2$  splitting)° with a step width of 0.05° and a scan speed of 0.02°/s. A total of 4746 reflections were recorded (5° <  $\theta$  < 57°). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent

computations, the Enraf-Nonius SDP/V18 package was used,<sup>33</sup> with the exception of a local data reduction program.

Three standard reflections measured every hour during the entire data collection period showed no significant trend in intensity. The raw step scan data were converted to intensities by using the Lehmann–Larson method<sup>34</sup> and then corrected for Lorentz, polarization, and absorption factors,<sup>35</sup> the latter computed by the numerical integration method of Busing and Levy<sup>36</sup> (transmission factors ranged between 0.076 and 0.331). A unique data set of 3814 reflections having  $I > 3\sigma(I)$  was used for determining and refining the structure.

The structure was solved by using the heavy-atom method. During structure determination it appeared that for each [(PPh<sub>3</sub>)Ru(DPF)( $\mu$ -Cl)Cl]<sub>2</sub> dimer, the unit cell contained two CHCl<sub>3</sub> solvent molecules. The chlorine atoms of these solvent molecules are disordered over two pairs of positions with respective occupancies of 0.75 and 0.25. After refinement of the heavy atoms, a difference-Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 7 Å<sup>2</sup> but not refined. Full least-squares refinement converged to  $R(F)$  = 0.069 and  $R_w(F)$  = 0.100 ( $w$  =  $1/\sigma^2(\text{count}) + (\rho)^2$ ). The unit weight observation was 2.00 for  $\rho$  = 0.08. A final difference map revealed no significant maxima.

Table VI lists the atomic positional and thermal parameters for all atoms with their estimated standard deviations.

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**Registry No.** 2 (M = W), 92097-49-9; 2 (M = Mo), 92125-55-8; 2 (M = Cr), 92097-52-4; 4, 92097-60-4; (DPF)[W(CO)<sub>5</sub>]<sub>2</sub>, 92097-50-2; (DPF)[Mo(CO)<sub>5</sub>]<sub>2</sub>, 92097-51-3; (DPF)[Cr(CO)<sub>5</sub>]<sub>2</sub>, 92097-53-5; (OC)<sub>5</sub>Mo(DPF)Cr(CO)<sub>5</sub>, 92097-54-6; (OC)<sub>5</sub>Mo(DPF)W(CO)<sub>5</sub>, 92097-55-7; (OC)<sub>5</sub>Cr(DPF)W(CO)<sub>5</sub>, 92097-56-8; (DPF)Mn<sub>2</sub>(CO)<sub>9</sub>, 92097-57-9; (DPF)[Mn<sub>2</sub>(CO)<sub>9</sub>]<sub>2</sub>, 92097-58-0; (DPF)<sub>2</sub>RuCl<sub>2</sub>, 92097-59-1; (DMPP)Cr(CO)<sub>5</sub>, 74363-90-9; (DMPP)Mo(CO)<sub>5</sub>, 74363-92-1; (DMPP)W(CO)<sub>5</sub>, 74363-95-4; (Ph<sub>3</sub>P)<sub>3</sub>RuCl<sub>2</sub>, 15529-49-4; Mn<sub>2</sub>(CO)<sub>10</sub>, 10170-69-1; Cr(CO)<sub>6</sub>, 13007-92-6; Mo(CO)<sub>6</sub>, 13939-06-5; W(CO)<sub>6</sub>, 14040-11-0.

**Supplementary Material Available:** Listings of hydrogen atomic coordinates, temperature factors, and observed and calculated structure factors (×10) (21 pages). Ordering information is given on any current masthead page.

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