Syntheses and Structures of Diruthenium Triple-Decker **Complexes with Bridging 1,2,4-Triphospholyl and** 1-Arsa-3,4-Diphospholyl Anions

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Yellow-brown oils, characterized spectroscopically as $[Cp*Ru(\eta^5-C_2-t-Bu_2P_3)]$, 11, and $[Cp*Ru(\eta^5-C_2-t-Bu_2AsP_2)]$, 12, were isolated from the reaction of $[Cp*Ru(CH_3CN)_3][PF_6]$, 6, with $[Li(C_2-t-Bu_2P_3)]$, 2, or $[Li(C_2-t-Bu_2AsP_2)]$, 4, respectively. Both 11 and 12 reacted further with **6** to give the triple-decker complexes $[Cp^*Ru(\mu-\eta^5:\eta^5-C_2-t-Bu_2P_3)RuCp^*][PF_6]$, **7**, and $[Cp*Ru(\mu-\eta^5;\eta^5-C_2-t-Bu_2AsP_3)RuCp*][PF_6]$, 8, in which the triphospholyl or arsadiphospholyl anions bridge two ruthenium centers. Both 7 and 8 have been characterized by singlecrystal X-ray crystal structure determinations. Crystal data for $C_{30}H_{48}F_6P_4Ru_2$, 7: M =848.7, $P_{2_12_12_1}$, a = 12.642(9) Å, b = 15.151(10 Å, c = 18.176(10) Å, V = 3481.4 Å³, $D_{calcd} = 12.642(9)$ Å, b = 15.151(10) Å, c = 18.176(10) Å, V = 3481.4 Å³, $D_{calcd} = 12.642(10)$ Å, b = 12.642(10) Å, b = 15.151(10) Å, c = 18.176(10) Å, V = 3481.4 Å³, $D_{calcd} = 12.642(10)$ Å, b = 15.151(10) Å, c = 18.176(10) Å, V = 3481.4 Å³, $D_{calcd} = 12.642(10)$ Å, b = 15.151(10) Å, c = 18.176(10) Å, V = 10.1642(10) Å, 1.62 g cm⁻³ (Z = 4) μ = 10.8 cm⁻¹ for Mo Ka radiation (λ = 0.7107 Å), final R = 0.055, $R_{\rm w}$ = 0.057, from 2716 observed reflections (3437 measured). Data for $C_{30}H_{48}AsF_6P_3Ru_2$, 8: M = 892.7, $P2_12_12_1$, a = 12.650(9) Å, b = 15.147(8) Å, c = 18.111(10) Å, V = 3470.1 Å³, D_{calcd} $= 1.71 \text{ g cm}^{-3} (Z = 4) \mu = 19.9 \text{ cm}^{-1}$ for Mo Ka radiation ($\lambda = 0.7107 \text{ Å}$), final $R = 0.049, R_w$ = 0.053, from 2760 observed reflections (3430 measured). Attempts to prepare mixed-metal triple-decker complexes by reacting $[Fe(\eta^5-C_5R_5)(\eta^5-C_2-t-Bu_2P_3)]$ (R = H, 14a; R = Me, 14b] or $[Fe(\eta^5-C_5R_5)(\eta^45-C_2-t-Bu_2AsP_2)]$ (R = H, 15a; R = Me, 15b) with 6 were unsuccessful. Likewise, when either 14a or 15a is treated with 6 the intermediate complexes [Fe(η^{5} -CN)2][PF6], 18, were isolated and spectroscopically characterized. When these were heated in nitromethane, a ring transfer occurred and the triple-decker species 7 or 8 was observed. Similar reactions involving 14b or 15b led directly to 7 or 8 without detection of any intermediate complexes.

Introduction

The synthesis of phospholyl anions of the type $C_n R_n P_{5-n}$ (n = 0-5) and their complexation to transition metals is a contemporary theme in the rapidly expanding area of phosphorus-carbon multiple-bond chemistry.^{2,3} Many mono- and polymetallic systems, containing a variety of coordination modes of phospholyl anions, have now been structurally characterized,² and the particular focus on this work is the study of complexes containing the di- and triphospholyl anions $[(C_3-t Bu_3P_2)^{-}$], 1, and $[(C_2-t-Bu_2P_3)^{-}]$, 2.³ Several polymetallic complexes in which 2 behaves as a bridging ligand are known,⁴⁻⁷ but so far no triple-decker complexes in which 2, or any other phospholyl anion, bridges two metals in a μ - η^5 : η^5 fashion have been isolated. There is one report by Grimes and co-workers⁸ of a triple-decker complex containing a terminal phospholyl ligand. In contrast, the triple-decker complexes $[Cp*Fe(\mu-\eta^5:\eta^5-E_5)FeCp*]$ -



 $[PF_6]$ (E = P, As), in which the pentaphospholyl **3a** or pentaarsolyl $3b^9$ anions bridge two Fe atoms, are known, as are homo- and heterobimetallic triple-decker complexes containing group 8 metals in which either Cp¹⁰ of Cp^{*11} ligand bridge the metals. The stability of 30-valence electron complexes of this type was predicted by Hoffman in 1976,¹² and calculations by Malar¹³ have

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Diruthenium Triple-Decker Complexes

shown the aromaticities of phosphorus-containing analogues of cyclopentadienyl anions are no less than 86% relative to $[C_5H_5^-]$; thus there seemed a strong likelihood for the possible synthesis of triple-decker complexes containing phospholyl anions by similar methods to those previously reported.

In this paper we describe the synthesis, characterization, and X-ray crystallographic studies of the diruthenium triple-decker complexes $[Cp^*Ru(\mu - \eta^5; \eta^5 - C_2 - t - Bu_2P_3) - t - Bu_2P_3]$ RuCp*][PF₆], 7, [Cp*Ru(μ - η^5 : η^5 -C₂-t-Bu₂AsP₂)RuCp*]- $[PF_6]$, 8, and $[Cp^*Ru(\mu \cdot \eta^5: \eta^5 \cdot C_2 \cdot t \cdot Bu_2PAsP)RuCp^*][PF_6]$, 9, in which 2 and the recently reported 14,15 1-arsa-3,4diphospholyl and 3-arsa-1,4-diphospholyl anions, 4 and 5, ligate in a μ - η^5 : η^5 mode. The attempted preparation of mixed-metal triple-decker complexes is also reported.

Results and Discussion

The synthesis of several iron complexes containing the anions 1 and 2 have been described, $4^{-7,16}$ and we have very recently reported the syntheses of several metal complexes containing the anions 4 and 5.14,15 Despite this, apart from a very recent paper by Mathey and coworkers,¹⁷ there has been little attention paid to phospholyl complexes of ruthenium. The CpRu derivatives of the anions 1 and 2 have been synthesized and characterized.¹⁸ and we now report the Cp*Ru derivatives of 1, 2, 4, and 5. Treatment of a 1.2-dimethoxyethane (DME) solution of $[Cp*Ru(CH_3CN)_3][PF_6]$, 6, with an equimolar amount of the lithium salt of either 2 or 4 gave the complexes [Cp*Ru(η^5 -C₂-t-Bu₂P₃)], 11, and $[Cp*Ru(\eta^5-C_2-t-Bu_2AsP_2)]$, 12, respectively (Scheme 1). Both compounds were characterized by NMR (¹H, ${}^{31}P{\{}^{1}H{\}})$ and mass spectroscopy. The ${}^{1}H$ NMR spectrum of 11 showed the expected two singlets due to Me and *t*-Bu protons. In addition to these signals, a weak singlet was observed, which was attributed to small amounts of $[Cp^*Ru(\eta^5-C_3-t-Bu_3P_2)]$, 10, which is formed due the unavoidable cosynthesis of 1 with $2.^{16}$

The ${}^{31}P{}^{1}H{}$ spectrum of 11 showed a triplet and doublet (J = 44 Hz), which is typical of ${}^{2}J_{P,P}$ coupling in metal complexes of $2^{4-6,16}$ A weak singlet also observed in this spectrum is attributed to 10. The ¹H NMR spectrum of 12 showed two singlets due to Cp* and t-Bu protons and several other signals in the Cp* and t-Bu regions. The ${}^{31}P{}^{1}H{}$ spectrum of 12 exhibited a singlet at δ 36.8 ppm, and several other resonances were also observed. Previous work¹⁴ has shown that the synthesis of pure 4 cannot be achieved and that small amounts of 1, 2, and 5 are always present. Thus the extra signals occurring in both the ¹H and ³¹P{¹H} spectra are attributed to $[Cp*Ru(\eta^5-C_2-t-Bu_2AsP)]$, 13, an isomer of 12, and to 10 and 11. The NMR spectroscopic data of complexes 10-13 are summarized in Table 1.



Table 1.	Selected ¹ H and ³¹ P NMR Spectroscopic
Data ^a	for New Mononuclear Phospholyl and
Arsadinh	ospholyl Compounds 10–13 and 15h–16h

compd	¹ H NMR δ (ppm)	³¹ P{ ¹ H} NMR δ (ppm)
10	1.60 (s, 18H); 1.87 (s, 15H)	21.8
11	1.39 (s, 18H); 1.80 (s, 15H)	18.0 (t); 36.2 (d)
		$[^{2}J_{P_{A},P_{X}} = 43.0 \text{ Hz}]$
12	1.39 (s, 18H); 1.80 (s, 15H)	36.8
13	1.38 (s, 18H); 1.79 (s, 15H)	16.3 (t); 66.7 (d)
		$[^{2}J_{P_{A},P_{X}} = 43.0 \text{ Hz}$
15b	1.49 (s, 18H); 1.70 (s, 15H)	49.9
16b	1.50 (s, 18H); 1.69 (s, 15H)	37.0 (t); 81.7 (d)
		$[{}^{2}J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}}) = 45.2 \mathrm{~Hz}]$

^a ¹H NMR: C₆D₆, 250 MHz. ³¹P{¹H} NMR: C₆D₆, 101.3 MHz.

When $[Cp*Ru(CH_3CN)_3][PF_6]$, 6, was treated with a 2-fold excess of either 2 or 4 or when complexes 10 or 11 were treated with 6, the novel triple-decker complexes $[Cp^*Ru(\mu - \eta^5: \eta^5 - C_2 - t - Bu_2P_3)RuCp^*][PF_6], 7, and$ $[Cp*Ru(\mu-\eta^5:\eta^5-C_2-t-Bu_2AsP_2)RuCp*][PF_6], 8$, were formed from the respective rections (Scheme 1). Prolonged heating of the reaction mixtures led to decomposition of the compexes. Both 7 and 8 were isolated as orange air-stable powders, soluble in THF, acetone, and chloroform but insoluble in ether and petroleum ether. The ¹H NMR spectra of both 7 and 8 showed, as expected, one resonance due to the Me protons and one resonance due to the *t*-Bu protons. In addition, the spectrum of $\mathbf{8}$ showed two resonances (δ 1.33 and 1.81) due the Me and t-Bu protons, respectively, of $[Cp^*Ru(\mu-\eta^5:\eta^5-C_2-t Bu_2PAsP$ $RuCp^*$ [PF₆], **9**, which was formed in addition to 8. A small amount of 7 was also detected in the ${}^{1}H$ NMR spectrum of 8, but this could be easily separated by fractional crystallization.

The ${}^{31}P{}^{1}H$ NMR spectrum of 7 showed an AX₂ pattern, $({}^{2}J_{P,P} = 36 \text{ Hz})$, shifted *ca*. 40 ppm upfield from the value observed for 11, as well as a septet due to the $[PF_6]^-$ anion. A similar upfield shift is observed when the complex $[Cp*Fe(\eta^5-P_5)]$ reacts with $[CpFe(C_6H_6)]$ - $[PF_6]$ to form $[Cp*Fe(\mu-\eta^5:\eta^5-P_5)FeCp][PF_6]$.⁸ Interestingly, no additional signals were observed in either the

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Table 2. Selected ¹H and ³¹P NMR Spectroscopic Data^a for New Dinuclear Phospholyl and
Arsadiphospholyl Compounds 7–9 and 17–19

compd	¹ H NMR δ (ppm)	$^{31}\mathrm{P}^{1}\mathrm{H}$ NMR δ (ppm)
7 8 9 17 18 19 ° ¹ H NMR	1.35 (s, 18H); 1.82 (s, 15H) 1.35 (s, 18H); 1.81 (s, 15H) 1.33 (s, 18H); 1.81 (s, 15H) 1.33 (s, 18H); 1.82 (s, 15H) 1.32 (s, 9H); 1.38 (s, 9H); 1.62 (s, 15H); 2.45 (s, 6H); 4.65 (s 1.37 (s, 9H); 1.43 (s, 9H); 1.62 (s, 15H); 2.47 (s, 6H); 4.65 (s 1.38 (s, 9H); 1.51 (s, 9H); 1.63 (s, 15H); 2.56 (s, 6H); 4.66 (s : CDCl ₃ , 250 MHz. ³¹ P{ ¹ H} NMR: CDCl ₃ , 101.3 MHz.	$\begin{array}{c} -2.37 \ (\mathrm{t}); -34.2 \ (\mathrm{d}) \ [^2J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}} = 37.0 \ \mathrm{Hz}] \\ -28.2 \\ 13.5 \ (\mathrm{d}); -40.9 \ (\mathrm{d}) \ [^2J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}} = 36.9 \ \mathrm{Hz}] \\ \mathrm{s}, 5\mathrm{H}) & -6.46 \ (\mathrm{P}_{\mathrm{A}}); 95.0 \ (\mathrm{P}_{\mathrm{B}}); 27.6 \ (\mathrm{P}_{\mathrm{C}}) \ [^1J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{B}}} = 437 \ \mathrm{Hz}, \\ \ ^2J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{C}}} = 47.0 \ \mathrm{Hz}, \ ^2J_{\mathrm{P}_{\mathrm{B}},\mathrm{P}_{\mathrm{C}}} = 48.3 \ \mathrm{Hz}] \\ \mathrm{s}, 5\mathrm{H}) & -5.20; 93.4 \ [^1J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}} = 447.0 \ \mathrm{Hz}] \\ \mathrm{s}, 5\mathrm{H}) & 23.2; 114.5 \ [^2J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}} = 50.1 \ \mathrm{Hz}] \end{array}$
C19 D	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C19 C14 C15 C10 C11 C16 C12 C17 C18 C18 C12 C17 C17 C18 C18 C12 C17 C17 C18 C18 C12 C17 C17 C18
C6 O-	$ \begin{array}{c ccccc} & & & & & & & & \\ & & & & & & & & \\ & & & &$	$C6 \qquad \bigcirc P2 \qquad \bigcirc P1 \qquad \bigcirc C2 \qquad \bigcirc C7 \qquad \bigcirc C10 \qquad \bigcirc P1 \qquad \bigcirc C2 \qquad \bigcirc C7 \qquad \bigcirc C7 \qquad \bigcirc C3 \qquad \bigcirc C1 \qquad As1 \qquad \bigcirc C6 \qquad \bigcirc C8 \qquad \bigcirc C6 \qquad \bigcirc C10 $



Figure 1. Molecular structure of compound 7.

¹H or ³¹P{¹H} NMR spectra of 7, indicating that complex 10 had not reacted any further with 6 to give the tripledecker species in which 1 is ligated in a μ - η^5 : η^5 fashion. This is probably due to the steric bulk of 1 since the presence of three *t*-Bu groups on the middle ring would inhibit coordination of two Cp*Ru fragments on either side of the ring. The ³¹P{¹H} NMR spectrum of 8 showed a singlet together with AX pattern (²J_{P,P} = 36 Hz) assigned to 9. In agreement with previous observations, both sets of signals are shifted *ca*. 60 ppm upfield relative to their parent complexes. Selected NMR spectroscopic data of complexes 7–9 are shown in Table 2.

The molecular structures of both 7 (Figure 1) and 8 (Figure 2) have been determined by single-crystal X-ray crystallographic studies and confirm the conclusions from the spectroscopic data. Interesting structural features of these complexes are the large dihedral angles between the Cp* rings and the middle ring (10.0° average for 7) and (10.4° average for 8), which are considerably bigger than those observed in the tripledecker complexes containing Cp or Cp* rings (typically about 2°)^{10,11} (see Tables 3–6). These larger values could be attributed to the presence of bulky *t*-Bu substituents in the middle ring which would push out the Cp* rings on either side. A similarly high value (8.1°) is observed in the structurally related complex



Figure 2. Molecular structure of compound 8.

 $[\operatorname{Ru}(\eta^5-\operatorname{C}_2-t-\operatorname{Bu}_2\operatorname{P}_3)_2]$ which has recently been synthesized.¹⁸ The two capping Cp* ligands in both complexes 7 and 8 are mutually eclipsed, and this orientation is consistent with other triple-decker species containing group 8 metals whose middle deck is either a Cp or Cp* ligand.^{10,11b} The bond lengths within the middle ring of 7 are slightly longer than the bond lengths observed in $[Ru(\eta^5-C_2-t-Bu_2P_3)_2]$,¹⁸ and interestingly Scherer et al. report a similar small increase in the bond lengths of both the P_5^- and As_5^- ligands when their ligation mode changes from η^5 to μ - η^5 : η^5 .^{8,9} An additional structural feature of **7** concerns the bond lengths between the each Ru atom and the center of the middle ring, (1.794 and 1.787 Å), which are marginally shorter than the bond length of 1.814 Å observed [Ru(η^5 -C₂-t- $Bu_2P_3)_2].^{18}$ No comparison of the bond distances in complex 8 can be made due to the lack of structurally characterized complexes containing arsadiphospholyl anions. The average bond distances from each Ru atom to the C atoms in the Cp* ligands is 2.20 Å in 7 and 2.21 Å in 8. These are slightly longer than those bond lengths observed in both decamethylruthenocene (2.17 $Å)^{19}$ and ruthenocene (2.186 Å).²⁰ A high disorder of

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Table 3. Fractional Atomic Coordinates andEquivalent Thermal Parameters for Compound 7

	x	у	z	$U_{ m eq}{}^a$
Ru (1)	0.87452(8)	0.80285(7)	0.26508(6)	0.032(1)
Ru(2)	0.67531(8)	0.96270(7)	0.30711(5)	0.031(1)
P(3)	0.6939(3)	0.7990(2)	0.3220(2)	0.039(2)
P(1)	0.8674(3)	0.9503(2)	0.3174(2)	0.038(2)
P(2)	0.7963(3)	0.9308(2)	0.2068(2)	0.036(2)
P(4)	0.7985(4)	0.5045(4)	0.9744(2)	0.072(3)
F (1)	0.8643(11)	0.4210(8)	0.9546(7)	0.147(10)
F (2)	0.8935(12)	0.5584(10)	0.9588(9)	0.188(12)
F (3)	0.8258(14)	0.4986(11)	1.0531(6)	0.197(13)
F(4)	0.7747(12)	0.5090(15)	0.8933(7)	0.240(15)
F(5)	0.7361(12)	0.5865(9)	0.9970(10)	0.185(13)
F(6)	0.7021(11)	0.4511(12)	0.9840(10)	0.292(14)
C(1)	0.7045(9)	0.8435(7)	0.2306(7)	0.033(6)
C(2)	0.7902(9)	0.8682(9)	0.3652(7)	0.036(7)
C(3)	0.6309(11)	0.8033(9)	0.1713(7)	0.046(7)
C(4)	0.6550(12)	0.7059(10)	0.1619(9)	0.069(10)
C(5)	0.5145(11)	0.8108(11)	0.1944(9)	0.061(9)
C(6)	0.6429(12)	0.8494(11)	0.0968(8)	0.065(10)
C(7)	0.8076(11)	0.8554(10)	0.4496(7)	0.046(8)
C(8)	0.8347(23)	0.9404(14)	0.4829(9)	0.126(17)
C(9)	0.7076(16)	0.8240(18)	0.4859(9)	0.124(16)
C(10)	0.8852(22)	0.7923(16)	0.4662(9)	0.187(18)
C(11)	0.9851(9)	0.6917(9)	0.2958(8)	0.044(7)
C(12)	1.0423(10)	0.7752(8)	0.2824(7)	0.043(8)
C(13)	1.0250(10)	0.7956(8)	0.2076(7)	0.044(7)
C(14)	0.9547(10)	0.7343(8)	0.1744(7)	0.038(7)
C(15)	0.9300(11)	0.6707(9)	0.2293(8)	0.051(8)
C(16)	0.9966(12)	0.6329(10)	0.3628(8)	0.060(9)
C(17)	1.1214(11)	0.8215(9)	0.3337(9)	0.061(9)
C(18)	1.0809(12)	0.8715(10)	0.1647(8)	0.063(9)
C(19)	0.9318(13)	0.7248(11)	0.0926(8)	0.064(10)
C(20)	0.8714(12)	0.5829(8)	0.2187(9)	0.058(9)
C(21)	0.5106(9)	1.0085(9)	0.3276(8)	0.046(8)
C(22)	0.5505(11)	1.0493(9)	0.2614(7)	0.048(8)
C(23)	0.6403(11)	1.0997(8)	0.2808(7)	0.045(8)
C(24)	0.6530(11)	1.0911(9)	0.3592(8)	0.052(9)
C(25)	0.5727(12)	1.0360(10)	0.3844(8)	0.059(9)
C(26)	0.4079(10)	0.9571(11)	0.3344(10)	0.076(11)
C(27)	0.5002(13)	1.0542(12)	0.1844(8)	0.092(11)
C(28)	0.7042(12)	1.1586(10)	0.2319(10)	0.083(10)
C(29)	0.7300(13)	1.1493(12)	0.4031(10)	0.079(11)
C(30)	0.5431(14)	1.0241(12)	0.4673(8)	0.080(10)

 a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

occupancy between the P and As atoms in the middle ring of **8** results from the cocrystallization of **8** and **9** from solution. This is not unexpected, as a similar disorder of occupany in both arsaphospholyl and arsadiphospholyl rings is observed in the structurally characterized complexes $[Fe(\eta^5-C_3Et_2HPAs)_2]^{21}$ and $[CpFe-(\eta^5-C_2-t-Bu_2AsP_2)W(CO)_5]^{.14}$

Surprisingly, the analogous diiron triple-decker complexes [Cp*Fe(μ - η^5 : η^5 -C₂-t-Bu₂P₃)FeCp*][PF₆] and [Cp*-Fe(μ - η^5 : η^5 -C₂-t-Bu₂AsP₂)FeCp*][PF₆] could not be prepared from the reaction of either [Cp*Fe(η^5 -C₂-t-Bu₂P₃)], **14b**, or [Cp*Fe(η^5 -C₂-t-Bu₂AsP₂)], **15b**, with [(C₅R₅)Fe-(C₆H₆)][PF₆], (R = H, Me), even after prolonged reflux of the rection mixtures. In such reactions the starting materials were recovered quantitatively, and UV irradiation of the reaction mixtures only resulted in decomposition. In contrast, triple-decker complexes containing As₅ or P₅ rings as the bridging ligands are readily synthesized by visible-light irradiation of [η^5 -CpFe(C₆H₆)][PF₆] and either (η^5 -C₅Me₄R)Fe(η_5 -As₅)] or [(η^5 -C₅Me₄R)Fe(η^5 -P₅)] (R = Me, Et).^{8,9} It is unclear why these types of diiron triple-decker complexes containing

Table 4.Fractional Atomic Coordinates andEquivalent Thermal Parameters for Compound 8

	x	у	z	$U_{ m eq}{}^a$
Ru(1)	0.87450(8)	0.79930(6)	0.26492(5)	0.032(1)
Ru(2)	0.67581(8)	0.95852(6)	0.30782(5)	0.031(1)
As	0.69172(13)	0.78976(11)	0.32575(8)	0.032(1)
P(1)	0.87005(21)	0.94954(17)	0.31694(15)	0.034(1)
P(2)	0.79574(21)	0.92827(17)	0.20397(15)	0.034(1)
P(3)	0.79730(33)	0.50138(34)	0.97332(24)	0.075(3)
F (1)	0.8626(10)	0.4194(7)	0.9513(6)	0.136(9)
F(2)	0.8936(11)	0.5572(8)	0.9597(7)	0.158(10)
F(3)	0.8304(15)	0.4973(9)	1.0521(6)	0.203(13)
F(4)	0.7720(12)	0.5060(15)	0.8914(7)	0.244(14)
F(5)	0.7353(11)	0.5838(9)	0.9971(9)	0.176(11)
F(6)	0.6983(11)	0.4476(11)	0.9850(10)	0.298(13)
C(1)	0.7035(9)	0.8386(7)	0.2311(6)	0.034(6)
C(2)	0.7944(6)	0.8685(8)	0.3665(6)	0.036(6)
C(3)	0.6291(10)	0.7998(8)	0.1705(6)	0.043(6)
C(4)	0.6520(12)	0.7007(10)	0.1609(9)	0.072(10)
C(5)	0.5151(10)	0.8037(10)	0.1972(8)	0.063(8)
C(6)	0.6412(13)	0.854(11)	0.0953(7)	0.078(10)
C(7)	0.8128(10)	0.8573(9)	0.4508(7)	0.051(7)
C(8)	0.8425(20)	0.9448(13)	0.4847(9)	0.133(15)
C(9)	0.7152(17)	0.8304(20)	0.4871(9)	0.162(20)
C(10)	0.9038(21)	0.7994(15)	0.4666(10)	0.178(18)
C(11)	0.9875(9)	0.6888(8)	0.2969(7)	0.045(7)
C(12)	1.0446(10)	0.7723(8)	0.2828(7)	0.044(7)
C(13)	1.0237(9)	0.7937(8)	0.2060(7)	0.048(7)
C(14)	0.9538(10)	0.7295(8)	0.1733(7)	0.049(8)
C(15)	0.9305(9)	0.6673(8)	0.2311(7)	0.042(7)
C(16)	0.9991(12)	0.6286(9)	0.3621(8)	0.063(9)
C(17)	1.1199(10)	0.8190(8)	0.3324(8)	0.056(8)
C(18)	1.0785(11)	0.8687(9)	0.1641(8)	0.070(9)
C(19)	0.9294(13)	0.7198(10)	0.0907(7)	0.067(10)
C(20)	0.8712(11)	0.5807(7)	0.2186(7)	0.051(7)
C(21)	0.5097(9)	1.0030(8)	0.3281(8)	0.049(8)
C(22)	0.5510(10)	1.0438(8)	0.2612(7)	0.045(7)
C(23)	0.6409(10)	1.0941(8)	0.2805(8)	0.050(8)
C(24)	0.6543(10)	1.0866(9)	0.3604(8)	0.055(8)
C(25)	0.5734(10)	1.0323(9)	0.3886(7)	0.049(7)
C(26)	0.4076(11)	0.9546(11)	0.3358(11)	0.088(11)
C(27)	0.5012(14)	1.0499(10)	0.1842(8)	0.095(10)
C(28)	0.7048(11)	1.1530(9)	0.2293(9)	0.077(9)
C(29)	0.7308(13)	1.1454(11)	0.4046(10)	0.095(11)
C(30)	0.5463(14)	1.0227(12)	0.4694(8)	0.097(11)

 a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

 $\eta^{5}\text{-}(\mathrm{C}_2\text{-}t\text{-}\mathrm{Bu}_2\mathrm{P}_3)$ and $\eta^{5}\text{-}(\mathrm{C}_2\text{-}t\text{-}\mathrm{Bu}_2\mathrm{AsP}_2)$ rings do not also form in this way, although diiron triple-decker species with bridging Cp* ligands have previously been found to be less stable than their Ru analogues.^{11a} It is possible that the triple-decker species [Cp*Fe(μ - $\eta^5:\eta^5\text{-}\mathrm{C}_2\text{-}t\text{-}\mathrm{Bu}_2\mathrm{P}_3$)FeCp*][PF6] and [Cp*Fe(μ - $\eta^5:\eta^5\text{-}\mathrm{C}_2\text{-}t\text{-}\mathrm{Bu}_2\mathrm{AsP}_2$)-FeCp*][PF6] were formed in the above reactions, but the presence of displaced benzene induced degradation of the triple-decker species. A similar reaction in which benzene degrades diruthenium triple-decker complexes is known.^{10}

The reaction of either $[CpFe(\eta^5-C_2-t-Bu_2P_3)]$, 14a, or $[CpFe(\eta^5-C_2-Bu_2AsP_2)]$, 15a, with $[Cp^*Ru(CH_3CN)_3]$ -[PF₆], 6, did not lead to the expected mixed-metal tripledecker species. Instead, displacement of one acetonitrile ligand from 5 resulted in the formation of the new mixed-metallic complexes $[CpFe(\eta^5-C_2-t-Bu_2P_3)Ru-(Cp^*)(CH_3CN)_2][PF_6]$, 17, and $[CpFe(\eta^5-C_2-t-Bu_2P_3)Ru-(Cp^*)(CH_3CN)_2][PF_6]$, 18, respectively (Scheme 2). The compounds were identified on the basis of NMR spectroscopy (Table 2). The ¹H NMR spectrum of 17 showed two signals that can be assigned to *t*-Bu protons, one signal from the CH₃CN protons and one signal due to Cp protons. Similar resonances were observed in the ¹H NMR spectrum of 18, together with extra signals due

⁽²¹⁾ Sierra, M. L.; Charrier, C.; Mathey, F. Bull. Chim. Soc. Fr. **1993**, 130, 521.

 Table 5.
 Intramolecular Distances (Å) and Angles (deg) for Compound 7 with ESD's in Parentheses

 (a) Bond Distances

	(a) Donu I	Distances	
Ru(1) - P(3)	2.508(4)	Ru(1) - P(1) Pu(1) - C(1)	2.429(3)
Ru(1) - F(2) Ru(1) - C(2)	2.421(3) 2.330(12)	Ru(1) - C(1) Ru(1) - C(11)	2.322(12) 2.258(13)
Ru(1) - C(12)	2.185(13)	Ru(1) - C(13)	2.173(13)
Ru(1) - C(14)	2.196(12)	Ru(1) - C(15)	2.219(14)
$Ru(1)-M1^a$	1.794	$Ru(1)-M2^{b}$	1.840
Ru(2) - P(3)	2.506(4)	$\operatorname{Ru}(2) - P(1)$	2.443(4)
Ru(2) - P(2)	2.429(4)	Ru(2) - C(1)	2.309(12)
Ru(2) = C(2)	2.297(12)	Ru(2) = C(21) Ru(2) = C(22)	2.226(12)
Ru(2) = C(22) Ru(2) = C(24)	2.2141(14) 2.181(14)	Ru(2) = C(25) Ru(2) = C(25)	2.170(12) 2.211(15)
Ru(2) - M1	1.787	$R_{11}(2) - M3^{\circ}$	1.846
P(3) - C(1)	1.798(13)	P(3) - C(2)	1.789(13)
P(1) - P(2)	2.223(5)	P(1) - C(2)	1.804(13)
P(2)-C(1)	1.813(12)	P(4) - F(1)	1.556(14)
$\mathbf{P}(4) - \mathbf{F}(2)$	1.48(2)	P(4)-F(3)	1.473(12)
P(4) - F(4)	1.507(14)	P(4) - F(5)	1.53(2)
P(4) - F(6)	1.47(2)	C(1) - C(3)	1.55(2)
C(2) = C(7)	1.00(2) 1.59(2)	C(3) = C(4) C(3) = C(6)	1.02(2) 1.59(2)
C(7) - C(8)	1.00(2) 1.46(3)	C(3) - C(9)	1.50(2)
C(7) - C(10)	1.40(3)	C(11) - C(12)	1.48(2)
C(11) - C(15)	1.43(2)	C(11) - C(16)	1.52(2)
C(12) - C(13)	1.41(2)	C(12) - C(17)	1.54(2)
C(13) - C(14)	1.42(2)	C(13) - C(18)	1.56(2)
C(14) - C(15)	1.42(2)	C(14) - C(19)	1.52(2)
C(15) - C(20)	1.53(2)	C(21) - C(22)	1.44(2)
C(21) = C(25)	1.36(2)	C(21) - C(26) C(22) - C(27)	1.52(2) 1.54(2)
C(22) = C(23)	1.41(2) 1 $44(2)$	C(22) = C(27) C(23) = C(28)	1.04(2) 1.50(2)
C(24) - C(25)	1.39(2)	C(24) - C(29)	1.54(2)
C(25) - C(30)	1.56(2)	0(=1) 0(=0)	210 2(2)
	(b) Band	Angles	
$M1 - R_{11}(1) - M2$	(D) DONO 175 1	M1 = Rn(2) = M2	174 0
C(1) - P(3) - C(2)	97.8(6)	P(2) - P(1) - C(2)	97.2(4)
P(1)-P(2)-C(1)	98.0(4)	F(1) - P(4) - F(2)	88.3(8)
F(1) - P(4) - F(3)	92.9(8)	F(1) - P(4) - F(4)	85.3(9)
F(1) - P(4) - F(5)	177.6(9)	F(1) - P(4) - F(6)	91.3(9)
F(2) - P(4) - F(3)	91.7(9)	F(2) - P(4) - F(4)	87.0(9)
F(2) - P(4) - F(5) F(2) - D(4) - F(4)	91.2(8)	F(2) - P(4) - F(6) F(2) - P(4) - F(5)	176(1)
F(3) = P(4) = F(4) F(3) = P(4) = F(4)	178(1)	F(3) = P(4) = F(5) F(3) = P(4) = F(5)	84.8(9)
F(3) - P(4) - F(6)	93(1)	F(4) - P(4) - F(5)	97(1)
F(4) - P(4) - F(6)	89(1)	F(5) - P(4) - F(6)	89.3(9)
P(3)-C(1)-P(2)	122.9(7)	P(3)-C(1)-C(3)	116.8(8)
P(2)-C(1)-C(3)	120.3(9)	P(3)-C(2)-P(1)	124.1(7)
P(3)-C(2)-C(7)	117.0(9)	P(1)-C(2)-C(7)	118.9(9)
C(1) - C(3) - C(4)	110(1)	C(1) - C(3) - C(5)	111(1)
C(1) = C(3) = C(6) C(4) = C(3) = C(6)	112(1) 109(1)	C(4) = C(3) = C(5) C(5) = C(3) = C(6)	107(1) 108(1)
C(4) = C(3) = C(6) C(2) = C(7) = C(8)	109(1)	C(3) = C(3) = C(6) C(2) = C(7) = C(9)	100(1) 111(1)
C(2) - C(7) - C(10)	113(1)	C(2) = C(7) - C(9)	107(2)
C(8) - C(7) - C(10)	110(2)	C(9) - C(7) - C(10)	106(2)
C(12)-C(11)-C(15)	107(1)	C(12)-C(11)-C(16)	126(1)
C(15)-C(11)-C(16)	126(1)	C(11)-C(12)-C(13)	106(1)
C(11) - C(12) - C(17)	128(1)	C(13)-C(12)-C(17)	126(1)
C(12)-C(13)-C(14)	111(1)	C(12) - C(13) - C(18)	125(1)
C(14) = C(13) = C(18) C(13) = C(14) = C(19)	124(1) 197(1)	C(13) = C(14) = C(15) C(15) = C(14) = C(19)	100(1) 195(1)
C(11) - C(15) - C(14)	110(1)	C(11) - C(15) - C(20)	120(1) 122(1)
C(14) - C(15) - C(20)	127(1)	C(22)-C(21)-C(25)	107(1)
C(22)-C(21)-C(26)	126(1)	C(25)-C(21)-C(26)	126(1)
C(21) - C(22) - C(23)	108(1)	C(21)-C(22)-C(27)	129(1)
C(23) - C(22) = C(27)	122(1)	C(22)-C(23)-C(24)	107(1)
C(22) = C(23) = C(28) C(23) = C(24) = C(25)	127(1) 107(1)	C(24) = C(23) = C(28) C(23) = C(24) = C(20)	126(1) 199(1)
C(25) - C(24) - C(25)	129(1)	C(23) = C(24) = C(29) C(21) = C(25) = C(24)	122(1) 111(1)
C(21) = C(25) = C(20)	194(1)	C(24) = C(25) = C(20)	194(1)

 a M1 is the centroid of the P(1)–P(2)–P(3)–C(1)–C(2) ring. b M2 is the centroid of the C(11)–C(15) ring. c M3 is the centroid of the C(21)–C(25) ring.

to the isomer of 18, $[CpFe(\eta^5-C_2-t-Bu_2PAsP)Ru(Cp^*)-(CH_3CN)_2][PF_6]$, 19. The ³¹P{¹H} NMR spectrum of 17 showed, as expected, an ABC pattern (¹J_{PA,PB} = 437 Hz,

Table 6. Intramolecular Distances (Å) and Angles(deg) for Compound 8 with ESD's in Parentheses

	Jound C Wi	ui ESD s in i ai	entireses
	(a) Bond I	Distances	
Ru(1)-As	2.565(2)	Ru(1) - P(1)	2.464(3)
Ru(1) - P(2)	2.455(3)	$\mathbf{Ru}(1) - \mathbf{C}(1)$	2.325(11)
Bu(1) - C(2)	2.347(11)	$B_{1}(1) - C(11)$	2.976(12)
Ru(1) = C(12)	2.047(11) 2.047(11)	$P_{11}(1) = C(12)$	2.270(12) 9.170(19)
Ru(1) = C(12)	2.210(12)	Ru(1) = C(13)	2.170(12)
Ru(1) - C(14)	2.209(13)	Ru(1) - C(15)	2.208(12)
Ru(2)-As	2.584(2)	$\operatorname{Ru}(2) - P(1)$	2.466(3)
Ru(2) - P(2)	2.460(3)	Ru(2) - C(1)	2.313(11)
Ru(2) - C(2)	2.288(11)	Ru(2) - C(21)	2.236(12)
Ru(2) - C(22)	2.207(12)	Ru(2) - C(23)	2.158(12)
Ru(2) - C(24)	2.179(14)	$R_{11}(2) - C(25)$	2 250(13)
$R_{1}(1) - M_{1q}^{a}$	1 8/1	$\mathbf{B}_{\mathbf{u}}(1) - \mathbf{M}\mathbf{S}^{c}$	1 709
$\mathbf{D}_{\mathbf{u}}(1) = \mathbf{M}_{0}$	1.041	$D_{u}(0) M_{0}$	1.792
$\operatorname{Ru}(2) = \operatorname{M2}^{\circ}$	1.039	Ru(2) - M3	1.782
As-C(1)	1.873(11)	As-C(2)	1.911(11)
P(1) - P(2)	2.275(4)	P(1) - C(2)	1.796(12)
P(2) - C(1)	1.856(11)	P(3) - F(1)	1.543(12)
P(3) - F(2)	1.503(14)	P(3) - F(3)	1.489(12)
P(3) - F(4)	1.520(14)	P(3) - F(5)	1.536(14)
P(3) - F(6)	1.51(2)	C(1) - C(3)	1.56(2)
C(2) - C(7)	1.55(9)	C(3) - C(4)	1.50(2) 1.54(9)
C(2) = C(1)	1.00(2) 1.51(0)	O(3) = O(4)	1.04(2)
U(7) = U(8)	1.51(2)	C(7) = C(9)	1.46(2)
C(7) - C(10)	1.47(3)	C(11) - C(12)	1.48(2)
C(11) - C(15)	1.43(2)	C(11) - C(16)	1.50(2)
C(12) - C(13)	1.45(2)	C(12) - C(17)	1.49(2)
C(13) - C(14)	1.44(2)	C(13) - C(18)	1.53(2)
C(14) - C(15)	1.44(2)	C(14) - C(19)	1.53(2)
C(15) = C(20)	1 59(9)	C(21) - C(22)	1.00(2) 1.46(2)
C(13) = C(20)	1.00(2)	C(21) = C(22)	1.40(2)
C(21) = C(25)	1.43(2)	C(21) - C(26)	1.49(2)
C(22) - C(23)	1.41(2)	C(22) - C(27)	1.53(2)
C(23) - C(24)	1.46(2)	C(23) - C(28)	1.52(2)
C(24) - C(25)	1.41(2)	C(24) - C(29)	1.54(2)
C(25) - C(30)	1.51(2)		
	(b) Bond	Angles	
M1 - Ru(1) - M3	174 9	$M_{2}^{0} - B_{11}(2) - M_{3}^{0}$	174 9
$C(1) = A_{0} = C(2)$	02.0(5)	D(2) = D(1) = C(2)	07 6(4)
D(1) = AS = C(2)	93.0(3)	F(2) = F(1) = C(2)	97.0(4)
P(1) = P(2) = U(1)	97.2(4)	F(1) - P(3) - F(2)	88.6(7)
F(1) - P(3) - F(3)	93.7(8)	F(1) - P(3) - F(4)	84.1(9)
F(1) - P(3) - F(5)	178.0(8)	F(1) - P(3) - F(6)	92.7(8)
F(2) - P(3) - F(3)	87.3(9)	F(2) - P(3) - F(4)	89.1(8)
F(2) - P(3) - F(5)	90.2(7)	F(2) - P(3) - F(6)	177.8(9)
F(3) - P(3) - F(4)	176(1)	F(3) - P(3) - F(5)	84 7(9)
F(3) - P(3) - F(6)	94(1)	F(4) - P(3) - F(5)	97(1)
F(A) - P(3) - F(6)	99(1)	F(5) = D(2) = F(6)	00 6(0)
F(4) = F(3) = F(0)	105 (1)	F(3) = F(3) = F(6)	00.0(0)
As = C(1) = P(2)	125.6(6)	As - C(1) - C(3)	116.5(8)
P(2) - C(1) - C(3)	117.9(8)	As - C(2) - P(1)	126.6(6)
As-C(2)-C(7)	114.4(8)	P(1)-C(2)-C(7)	119.0(8)
C(1)-C(3)-C(4)	109(1)	C(1) - C(3) - C(5)	109(1)
C(1)-C(3)-C(6)	113(1)	C(4) - C(3) - C(5)	105(1)
C(4) - C(3) - C(6)	109(1)	C(5) - C(3) - C(6)	111(1)
C(2) - C(7) - C(8)	110(1)	C(2) - C(7) - C(9)	110(1)
C(2) = C(7) = C(10)	119(1)	C(2) = C(7) = C(0)	106(2)
C(2) = C(7) = C(10) C(2) = C(7) = C(10)	112(1)	C(0) = C(7) = C(9)	100(2)
C(8) = C(7) = C(10)	104(1)	C(9) = C(7) = C(10)	114(2)
C(12) - C(11) - C(15)	107(1)	C(12) - C(11) - C(16)) 127(1)
C(15)-C(11)-C(16)	125(1)	C(11)-C(12)-C(13)) 105(1)
C(11)-C(12)-C(17)	128(1)	C(13) - C(12) - C(17)) 126(1)
C(12)-C(13)-C(14)	111(1)	C(12)-C(13)-C(18)) 124(1)
C(14) - C(13) - C(18)	125(1)	C(13) - C(14) - C(15)	106(1)
C(13) - C(14) - C(19)	126(1)	C(15) - C(14) - C(10)	127(1)
C(11) = C(15) = C(14)	111(1)	C(11) = C(15) = C(10)	194(1)
O(14) = O(10) = O(14) O(14) = O(15) = O(00)	104(1)	O(11) = O(10) = O(20)	124(1)
U(14) = U(10) = U(20)	124(1)	U(22) = U(21) = U(25)	108(1)
U(22) = U(21) = U(26)	127(1)	U(25) - U(21) - U(26)) $125(1)$
C(21) - C(22) - C(23)	108(1)	C(21) - C(22) - C(27)) 129(1)
C(23) - C(22) - C(27)	122(1)	C(22)-C(23)-C(24)) 107(1)
C(22) - C(23) - C(28)	126(1)	C(24)-C(23)-C(28)) 126(1)
C(23)-C(24)-C(25)	109(1)	C(23)-C(24)-C(29)) 123(1)
C(25)-C(24)-C(29)	127(1)	C(21)-C(25)-C(24)	108(1)
C(21) - C(25) - C(30)	126(1)	C(24) - C(25) - C(30)	125(1)

 a M1 is the centroid of the C(11)–C(15) ring. b M2 is the centroid of the C(21)–C(25) ring. c M3 is the centroid of the As–P(1)–P(2)–C(1)–C(2) ring.

 ${}^{2}J_{PA,PC} = 44.7 \text{ Hz}, {}^{2}J_{PB,PC} = 50.1 \text{ Hz}$), the magnitude of the coupling constants being similar to those previously reported for $\eta^{5:1}$ -ligated (C₂-*t*-Bu₂P₃) rings.⁴⁻⁷ Two resonances were observed in the ${}^{31}P{}^{1}H{}$ NMR spectrum of **18** (${}^{1}J_{PA,PB} = 447 \text{ Hz}$), the large coupling constant



Unknown Fe products

clearly showing that the two adjacent P atoms of C_2 -t- Bu_2P_3 ring are *both* coordinated. Also observed in this spectrum was a set of signals showing an AX pattern $(^{2}J_{PA,PX} = 50.1 \text{ Hz})$ which arise from complex 19. A similar attempt to prepare mixed-metal triple-decker complexes from the reaction of $[Cp^*Fe(\eta^5-C_2-t-Bu_2P_3)]$, **14b**, or $[Cp*Fe(\eta^5-C_2-t-Bu_2AsP_2)]$, **15b**, with **6** led to the direct formation of the triple-decker species 7 and 8, respectively (Scheme 2), as evidenced by their typical ³¹P{¹H} NMR spectra. Also present in the reaction mixtures was the ruthenium species $[Cp^*Ru(\eta^5-C_2-t Bu_2P_1$], 11, or [Cp*Ru(η^5 -C₂-t-Bu₂AsP₂)], 12, respectively, both of which were easily separated from the tripledecker complexes. Both 7 and 8 were also formed by heating nitromethane solutions of either 17 or 18. Monitoring these reactions by ³¹P{¹H} NMR spectroscopy showed complexes 7 or 8 and 11 or 12 to be present. Thus from these detailed studies it is apparent that a ring-transfer reaction of the phospholyl or arsadiphospholyl ligands from the Fe atom to the Ru atom is taking place in each case.

These types of ring-transfer reactions were first identified by Maitlis et al.²² and are particularly useful for the preparation of a variety of new metal cyclobutadiene complexes.^{23,24} The mechanism of these reactions was first thought to proceed via monofacially bridged bimetallic species,²³ and the structural characterization of the monofacially-bridged Pd₂ complex, [Pd₂(Al₂Cl₇)₂- $(\mu - \eta^6 - C_6 H_6)_2]$,²⁵ strengthened this theory. However, similar cyclobutadiene species remained uncharacterized, and thus the mechanism is unproven. A second proposed mechanism, particularly for the ring transfer of η^5 -borole ligands, has been suggested by Herberich et al.^{26,27} This involves the formation of bifacially bridged (triple-decker) species by electrophilic stacking and subsequent decomposition by nucleophilic degradation with the ring being transferred from one metal to the other.

In a very recent paper, Herberich and Jansen²⁸ have established the intermediacy of this type of triple-decker complex in cyclopentadienyl ring-transfer reactions, in particular in the stereospecific transfer of isodicyclopentadienyl ligands from ruthenium to rhodium. In the case of the present study involving the transfer of phospholyl or arsadiphospholyl ligands, the Herberich mechanism also appears to be applicable. Thus the dinuclear complexes 17 or 18 might lose acetonitrile in refluxing nitromethane to give either [Cp*Fe(μ - η^5 : η^5 - $C_2-t-Bu_2P_3)RuCp*][PF_6] \text{ or } [Cp*Fe(\mu-\eta^5:\eta^5-C_2-t-Bu_2AsP_2) RuCp^*$][PF₆]. Alternatively the direct reaction of either $[Cp*Fe(\eta^{5}-C_{2}-t-Bu_{2}P_{3})], 14b, or [Cp*Fe(\eta^{5}C_{2}-t-Bu_{2}AsP_{2})],$ 15b, with $[Cp*Ru(CH_3CN)_3][PF_6]$, 6, would lead to the same products. These unstable species can then readily undergo nucleophilic degradation induced by displaced acetonitrile to give either $[Cp^*Ru(\eta^5-C_2-t-Bu_2P_3)]$, 11, or $[Cp*Ru(\eta^{5}-C_{2}-t-Bu_{2}AsP_{2})], 12, and [Cp*Fe(CH_{3}CN)_{3}]^{+}.$ The presence of the triple-decker species 7 and 8 in these reactions is explained by an excess of 6 reacting

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with either 10 or 11 (Scheme 2). No iron-containing products were detected in the reaction mixture even though the unstable $[CpFe(CH_3CN)_3]^+$ cation is known to readily decompose to ferrocene at room temperature.²⁹ Likewise, neither pentamethyl- nor decamethylferrocenes were detected in similar solvent-induced nucleophilic degradation reactions previously reported for iron/ruthenium mixed-metal triple-decker complexes containing bridging cyclopentadienyl ligands,¹⁰ and in this case a similar decomposition is believed to have occurred.

Conclusions

The formation of the diruthenium triple-decker complexes $[Cp*Ru(\mu-\eta^5:\eta^5-C_2-t-Bu_2P_3)RuCp*][PF_6], 7, and$ $[Cp*Ru(\mu-\eta^5:\eta^5-C_2-t-Bu_2AsP_2)RuCp*][PF_6], 8$, by an electrophilic stacking mechanism is similar to the syntheses of other triple-decker systems of group 8 metals containing a variety of non-phosphorus containing bridging ligands. The occurrence of a ring-transfer reaction in the attempted formation of mixed-metal triple-decker complexes containing bridging phospholyl and arsadiphospholyl ligands suggests that these complexes probably have also been formed; however, their instability has prevented any characterization. The lack of stability of such intermediates is probably due to the presence of donor solvents in the reaction mixture which enhance the rate of nucleophilic degradation. Alternative synthetic routes to mixed-metal species are currently under investigation, as is the ligating potential of the phosphorus atoms in the middle decks of the novel cationic diruthenium complexes 7 and 8 described in this paper.

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen gas using standard Schlenk techniques. The solvents 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), petroleum ether 60-80° fraction (hereafter referred to as petroleum ether), and diethyl ether (ether) were distilled from Na/K alloy before use. Acetone and dichloromethane were distilled from CaSO₄ and CaH₂, respectively, before use. All NMR spectra were recorded on a Bruker AC-P250 spectrometer at the following frequencies: ¹H, 250.1 MHz, C₆D₆ or CDCl₃ internal reference; ³¹P{¹H}, 101.3 MHz, 85% H₃PO₄ external reference, recorded in CDCl₃ unless otherwise stated. Mass spectra (EI) were recorded on a Kratos MS80RF instrument, and melting points were measured on an Electrothermal melting point apparatus and are uncorrected. All microanalyses were carried out by Miss Mita Patel at the University of Sussex. The starting materials $[Li(C_2-t-Bu_2P_3)], 2, {}^{16} [Li(C_2-t-Bu_2AsP_2)], 4, {}^{14}$ C_2 -t-Bu₂P₃)], 14b,⁶ [CpFe(η^5 -C₂-t-Bu₂P₃)], 14a,³ and [CpFe(η^5 - C_2 -t-Bu₂AsP₂)], 15a,¹⁴ were prepared by published procedures. The complex $[Cp*Fe(\eta^5-C_2-t-Bu_2AsP_2)]$, 15b, was prepared in a similar manner to $[Cp*Fe(\eta^5-C_2-t-Bu_2P_3)]$, 14b,⁶ as described below. All other reagents were used as received.

(Pentamethylcyclopentadienyl)(1-arsa-3,4-diphospha-2,5-di-tert-butylcyclopentadienyl)iron (15b). To a 10 cm^3 DME solution of [FeCl₂] (0.26 g, 2.0 mmol) were added a solution of [Li(C₅Me₅)] (2 mmol in 10 cm³ of THF) and a 5 cm³ DME solution of [Li(C₂-t-Bu₂AsP₂)], 4 (2 mmol). The reaction mixture was stirred for 5 h, during which time a deep-red solution formed. Removal of solvent *in vacuo* gave a brown oil, which was extracted twice with petroleum ether. The combined extracts were eluted down a kieselgel column with petroleum ether, and two bands were collected. The orange first band was identified by ¹H NMR spectroscopy as [Fe(C₅-Me₅)₂].³² The major red band was identified spectroscopically as a mixture of four complexes, namely, [Cp*Fe(η^{5} -C₂-t-Bu₂-AsP₂)], **15b** {¹H NMR (C₆D₆), δ 1.49 (s, t-Bu) 1.70 (s, C₅Me₅); ³¹P{¹H} NMR (CDCl₃), δ 49.9; MS (70 eV, EI) m/z 466 [M⁺, 40%], 328 [M⁺ - (t-BuC)₂, 40%]}, as the predominant product, its isomer [Cp*Fe(η^{5} -C₂-t-Bu₂PAsP)], **16b** {¹H NMR (C₆D₆), δ 1.50 (s, t-Bu), 1.69 (s, C₅Me₅); ³¹P{¹H} NMR (C₆D₆), (AX) δ 37.0 P_A, 81.7 P_X, ²J_{PA,PX} = 45.2 Hz}, and the previously reported⁵ complexes [Cp*Fe(η^{5} -C₂-t-Bu₂P₃)], **14b**, and [Cp*Fe(η^{5} -C₃-t-Bu₃P₂)]. Attempts to separate the individual components by fractional crystallization or sublimation were unsuccessful.

(Pentamethylcyclopentadienyl)(1,3,4-triphospha-2,5di-tert-butylcyclopentadienyl)ruthenium (11). A 10 cm³ DME solution of [Li(C2-t-Bu2P3)], 2 (1.0 mmol), was added slowly to 6 (0.45 g, 0.90 mmol) in DME (10 cm³), and the resulting brown solution was stirred for 3 h. All volatile components were removed in vacuo, and the residual oil was extracted twice with petroleum ether. The yellow oil obtained after removal of solvent could not be purified by column chromatography because of decomposition but was identified spectroscopically as $[Cp*Ru(\eta^5-C_2-t-Bu_2P_3)]$, 11 {¹H NMR $(C_6D_6) \delta 1.39 (s, t-Bu), 1.80 (s, C_5Me_5); {}^{31}P{}^{1}H} NMR (CDCl_3)$ $(AX_2) \delta 18.0 P_A, 36.2 P_X, {}^2J_{PA,PX} = 43.0 Hz; MS (70 eV, EI) m/z$ 468 [M⁺, 25%], 411 [M⁺ - t-Bu, 10%], 330 [M⁺ - (t-BuC)₂, 35%]}, together with a small amount of $[Cp*Ru(\eta^5-C_3-t-Bu_3P_2)]$, **10** {¹H NMR (C_6D_6) δ 1.60 (s, t-Bu), 1.87 (s, C_5Me_5); ³¹P{¹H} NMR (CDCl₃) δ 21.8}. The two products could not be separated by either fractional crystallization or sublimation.

(Pentamethylcyclopentadienyl)(1-arsa-3,4-diphospha-2,5-di-*tert*-butylcyclopentadienyl)ruthenium (12) was prepared in a similar manner from **6** (0.24 g, 0.48 mmol) and a 0.6 mmol solution of [Li(C₂-t-Bu₂AsP₂)], **4** {¹H NMR (C₆H₆) δ 1.39 (s, t-Bu), 1.80 (s, C₅Me₅); ³¹P{¹H} NMR (C₆D₆) δ 36.8; MS (70 eV, EI) m/z 511 [M⁺, 40%], 373 [M⁺ - (t-BuC)₂, 40%]}.

(Pentamethylcyclopentadienyl)(3-arsa-1,4-diphospha-2,5-di-*tert*-butylcyclopentadienyl)ruthenium (13), an isomer of 12, was also identified in the reaction products {¹H NMR (C_6D_6) δ 1.38 (s, *t*-Bu), 1.79 (s, C_5Me_5); ³¹P{¹H} NMR (C_6D_6) (AX) δ 16.3 P_A, 66.7 P_X, ²J_{PA,PX} = 43.0 Hz, as were 10 and 11, but these complexes could not be separated by sublimation or fractional crystallization.

(µ-1,3,4-Triphospha-2,5-di-tert-butylcyclopentadienyl)bis[(pentamethylcyclopentadienyl)ruthenium] Hexafluorophosphate (7). Both 6 (0.82 g, 1.60 mmol) and [Li(C₂-t-Bu₂P₃)], 2 (0.80 mmol), were stirred for 6 h in DME (20 cm³). All volatile components were then removed *in vacuo*, and the residual oil was washed with ether. The oil was taken up in THF and filtered through a 5 cm³ pad of alumina (neutral, activity I), and the resulting orange solution was evaporated to dryness. Treatment of the oil obtained with ether afforded 7 (0.15 g, 22%) as an orange powder, mp = 234 °C (decomp). Anal. Calcd for C₃₀H₄₈F₆P₄Ru₂: C, 42.4; H, 5.60. Found: C, 42.1; H, 4.90. ¹H NMR (CDCl₃) δ 1.35 (s, *t*-Bu), 1.81 (s, C₅Me₅); ³¹P{¹H} NMR (CDCl₃) (AX₂) δ -2.37 P_A, -34.2 P_X, ²J_{PA,PX} = 37.0 Hz, PF₆ -142.6 (sept, ¹J_{P,F} = 708 Hz).

(µ-1-Arsa-3,4-diphospha-2,5-di-*tert*-butylcyclopentadienyl)bis[(pentamethylcyclopentadienyl)ruthenium] hexafluorophosphate (8) was prepared in a similar manner from 6 (0.82 g, 1.60 mmol) and [Li(C₂-t-Bu₂AsP₂)], 4 (0.80 mmol), and isolated (0.08 g, 12%) as an orange powder, mp = 239 °C (decomp). Anal. Calcd for C₃₀H₄₈AsF₆P₃Ru₂: C. 40.5; H, 5.30. Found: C, 41.1; H, 4.90. ¹H NMR (CDCl₃) δ 1.35 (s, t-Bu), 1.81 (s, C₅Me₅); ³¹P{¹H} NMR (CDCl₃) δ -28.2, PF₆ -142.6 (sept, ¹J_{P,F} = 708 Hz).

 $(\mu$ -3-Arsa-1,4-diphospha-2,5-di-*tert*-butylcyclopentadienyl)bis[(pentamethylcyclopentadienyl)ruthenium]

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hexafluorophosphate (9), an isomer of 7, was also identified as a product from the above reaction {¹H NMR (CDCl₃) δ 1.33 (s, *t*-Bu), 1.81 (s, C₅*Me*₅); ³¹P{¹H} NMR (CDCl₃) (AX) δ 13.5 P_A, -40.9 P_X, ²*J*_{PA,PX} = 36.9 Hz, PF₆ -142.6 (sept, ¹*J*_{P,F} = 708 Hz)}, together with 7 which was separated by fractional crystallization.

Complexes **7–9** could also be prepared from the reactions of appropriate Cp*Fe precursors with [Cp*Ru(CH₃CN)₃][PF₆], **6**, in either DME or CH₂Cl₂, followed by workup as described above. In this way **7** was formed from [Cp*Fe($\eta^{5-C_2-t-Bu_2P_3}$]], **14b**, in 30% yield, and **8** and its isomer **9** were formed in 27% yield from [Cp*Fe($\eta^{5-C_2-t-Bu_2AsP_2}$]], **15b**, [Cp*Ru($\eta^{5-C_3-t-Bu_3P_2}$]], and [Cp*Fe($\eta^{5-C_2-t-Bu_2PAsP_3}$]], **16b**.

(Cyclopentadienyliron) (1, 3, 4-triphospha-2, 5-di-tertbutylcyclopentadienyl)(pentamethylcyclopentadienyl)bis(acetonitrile)ruthenium Hexafluorophosphate (17). A 30 cm³ CH₂Cl₂ solution of [CpFe(η^{5} -C₂-t-Bu₂P₃)], **14a** (0.11 g, 0.30 mmol), and [Cp*Ru(CH₃CN)₃][PF₆], 6, was stirred for 5 h while being irradiated with a 100 W light. Removal of solvent in vacuo left an orange oily residue, which was redissolved in acetone and filtered through alumina (neutral, activity I). The solvent was again removed to leave an oily solid, which was identified spectroscopically as $[CpFe(\eta^5-C_2$ *t*-Bu₂P₃)RuCp*(CH₃CN)₂][PF₆], **17** {¹H NMR (CDCl₃) δ 1.32 (s, t-Bu), 1.38 (s, t-Bu), 1.62 (s, C₅Me₅), 2.45 (CH₃CN), 4.65 (s, C₅ H_5); ³¹P{¹H} NMR (CDCl₃) (ABC) δ_{PA} 95.0, δ_{PB} 27.6, δ_{PC} -6.46, $J_{PA,PB} = 437$ Hz, $J_{PA,PC} = 47.0$ Hz, $J_{PB,PC} = 48.3$ Hz, $PF_6 - 142.9$ (sept, ${}^1J_{P,F} = 712$ Hz)}. The solid also contained a small, but inseparable, amount of 6, as identified by ¹H NMR spectroscopy; thus satisfactory microanalytical data could not be obtained.

(Cyclopentadienyliron)(1-arsa-3,4-diphospha-2,5-ditert-butylcyclopentadienyl)(pentamethylcyclopentadienyl)bis(acetonitrile)ruthenium hexafluorophosphate (18) was synthesized, as an oily solid, in a similar manner from 6 and [CpFe($\eta^{5-}C_2-t-Bu_2P_3$)], 14a. ¹H NMR (CDCl₃) δ 1.37 (s, t-Bu), 1.43 (s, t-Bu), 1.62 (s, C₅Me₅), 2.47 (CH₃CN), 4.65 (s, C₅H₅); ³¹P{¹H} NMR (CDCl₃) (AB) δ_{PA} –5.20, δ_{PB} 93.4, $J_{PA,PB}$ 447 Hz, PF₆ –145.4 (sept, ¹J_{P,F} = 712 Hz).

(Cyclopentadienyliron)(3-arsa-1,4-diphospha-2,5-ditert-butylcyclopentadienyl)(pentamethylcyclopentadienyl)bis(acetonitrile)ruthenium hexafluorophosphate (19), an isomer of 18, was also found to be present in the resulting solid. ¹H NMR (CDCl₃) δ 1.38 (s, *t*-Bu), 1.51 (s, *t*-Bu), 1.63 (s, C₅Me₅), 2.56 (CH₃CN), 4.66 (s, C₅H₅); ³¹P{¹H} NMR (CDCl₃) (AX) δ_{PA} 23.2, δ_{PX} 114.5, $J_{PA,PB}$ = 50.1 Hz, PF₆ -145.4 (sept, ${}^{1}J_{P,F} = 712$ Hz). Again 6 was found to be present, and thus a satisfactory microanalysis could not be obtained.

Crystallography for Complex 7. Crystal data for $C_{30}H_{48}F_6P_4Ru_2$; M = 848.7; space group $P2_12_12_1$ (No. 19); cell parameters a = 12.642(9) Å, b = 15.151(10) Å, c = 18.176(10) Å, V = 3481.4 Å³; Z = 4; $D_{calcd} = 1.62$ g cm⁻³; F(000) = 1720; $\mu = 10.8$ cm⁻¹ for Mo K α radiation ($\lambda = 0.7107$ Å), T = 293 K.

Structure Determination for 7. Single crystals of [Cp*Ru-(μ - η^{5} : η^{5} -C₂-t-Bu₂P₃)RuCp*][PF₆], **7**, were grown from chloroform/ pentane. The 3437 unique reflections were collected from an air-stable red crystal of dimensions *ca.* 0.2 × 0.2 × 0.1 mm³ on an Enraf-Nonius CAD4 in θ -2 θ mode for 2° < 2 σ < 25°, of which 2716 reflections had $|F^2| > 2\sigma(F^2)$. Structure solution was by heavy atom methods (SHELXS-86). A DIFABS absorption correction (max 1.15, min 0.88) was made; refinement by full-matrix least-squares with all heavy atoms anisotropic converged at R = 0.055, R' = 0.057.

Crystallography for Complex 8. Crystal data: $C_{30}H_{48}$ -AsF₆P₃Ru₂; M = 892.7; space group $P2_12_12_1$ (No. 19); a = 12.650(9) Å, b = 15.147(8) Å, c = 18.111(10) Å, V = 3470.1 Å³; Z = 4; $D_{calcd} = 1.71$ g cm⁻³; F(000) = 1792; $\mu = 19.9$ cm⁻¹ for Mo K α radiation ($\lambda = 0.7107$ Å), T = 293 K.

Structure Determination for 8. Single crystals of [Cp*Ru-(μ - $\eta^{5:}\eta^{5-}C_2$ -t-Bu₂AsP₂)RuCp*][PF₆], **8**, were grown from chloroform/pentane. The 3430 unique reflections were collected from an air-stable red crystal of dimensions ca. $0.25 \times 0.25 \times$ 0.05 mm^3 on an Enraf-Nonius CAD4 in θ - 2θ mode for $2^\circ < 2\sigma < 25^\circ$, of which 2760 had $|F^2| > 2\sigma(F^2)$. Structure solution was by heavy atom methods (SHELXS-86). A DIFABS absorption correction (max 1.15, min 0.91) was made; refinement by full-matrix least-squares with all heavy atoms anisotropic converged at R = 0.049, R' = 0.053. There is disorder between the P and As atoms such that the site labeled "As" has occupancy 0.5As + 0.5P and both P1 and P2 have occupancy 0.75P + 0.25As; appropriate averaged scattering factors were used.

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Supporting Information Available: Tables of anisotropic temperature factors for **7** and **8** (4 pages). Ordering information is given on any current masthead page.

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