to allow diffusion into the [IrCl(CO)(PPh$_3$)$_2$]/CD$_2$Cl$_2$ compartment and reaction to produce the known hydride, [IrH$_2$Cl(CO)(PPh$_3$)$_2$]. Indeed, weak signals were observed at −7.02 and −18.34 ppm, which suggest the presence of low levels of [IrH$_2$Cl(CO)(PPh$_3$)$_2$] in solution.[5] Additionally, a triplet at −15.28 ppm ($^2J_{P,H}$ = 11.4 Hz) was observed, which may be indicative of the presence of [IrHCl$_2$(CO)(PPh$_3$)$_2$] in solution.[6] The origin of this product is obscure but may be related to the presence of acidic impurities in the CD$_2$Cl$_2$ employed. Attempts to confirm the presence of these iridium hydrides by ^{31}P{^{1}H} NMR spectroscopy failed due to their very low concentrations.

In addition to the use of trapping experiments we sought to detect evolved hydrogen in the gas phase above a solution of [Pd$_2$Cl$_2$(μ-dmpm)$_2$] in CH$_3$NO$_2$ by Raman spectroscopy and by gas chromatography using a Porapak Q column. Neither of these experiments produced any positive evidence for hydrogen evolution. The NMR experiments are certainly suggestive of H$_2$ evolution in the reaction of [Pd$_2$Cl$_2$(μ-dmpm)$_2$] with CH$_3$NO$_2$, but some ambiguity clearly remains. The long time period over which the reaction occurs (several weeks near 0 °C) hinders definitive experiments.

Interestingly, the complex [Pd$_2$Cl$_2$(μ-dppm)$_2$] does not react with nitromethane under conditions comparable to those employed for the dmpm complex, **5**, indicating that the reaction of this substrate with d^9–d^9 dipalladium systems is sensitive to the steric and electronic properties of the ligand set.[7]

Given the differences in reactivity toward nitromethane of the d^9–d^9 dipalladium and digold complexes, **5** and **1**, it will be of interest to compare the reactions of the d^{10}–d^{10} dipalladium complexes, [Pd$_2$(diphosphine)$_3$], with those already reported for the d^{10}–d^{10} digold complex, **4**. Studies in this area are underway.

Experimental Section

The compounds [Pd$_2$Cl$_2$(μ-dppm)$_2$][8] and [IrCl(CO)(PPh$_3$)$_2$][9] were prepared by literature routes. [Pd$_2$Cl$_2$(μ-dmpm)$_2$] was prepared by ligand exchange of [Pd$_2$Cl$_2$(μ-dppm)$_2$] with dmpm.[10] NMR measurements were made on Varian VXR-400 and JEOL FX-90Q NMR spectrometers. IR measurements were made on a Nicolet 5DX FTIR spectrometer. Raman measurements were made by Dr. E. W. Findsen of this Department using equipment assembled in house. GC measurements were made on a Hewlett-Packard 5890 chromatograph equipped with a Porapak Q column.

Preparation of [Pd$_2$Cl$_2$(CH$_2$NO$_2$)$_2$(μ-dmpm)$_2$] (6). [Pd$_2$Cl$_2$(μ-dmpm)$_2$] (160 mg) was dissolved in CH$_3$NO$_2$ (12 mL), and the solution was stored in the freezer compartment of a refrigerator (ca. 0 °C) for 15 weeks, during which time light yellow crystals of **6** precipitated. Filtration and air-drying allowed isolation of **6** in 30% yield.

Crystallographic Studies. Crystal data are collected in Table I. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by the Patterson heavy-atom method, which revealed the position of one palladium atom. The remaining atoms were located via successive difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained as riding atoms. Final values of R = 0.032 and R_w = 0.039 were obtained. All calculations were performed on a VAX 11/750 computer using SDP-VAX. Full details are included in the supplementary material.

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Registry No. 5, 89178-59-6; 6, 134967-74-1; [Pd$_2$Cl$_2$(μ-dppm)$_2$], 64345-29-5; MeNO$_2$, 75-52-5.

Supplementary Material Available: A complete textural description of the data collection and refinement and tables of crystallographic data and thermal parameters (7 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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[5] Literature values are −7.3 and −18.4 ppm in CH$_2$Cl$_2$ solution, see: Taylor, R. C.; Young, J. F.; Wilkinson, G. *Inorg. Chem.* **1966**, *5*, 20.

[6] The same triplet is observed when [IrCl(CO)(PPh$_3$)$_2$] in CD$_2$Cl$_2$ is treated with concentrated HCl. The complex [IrHCl$_2$(CO)(PPh$_3$)$_2$] has been synthesized previously by the reaction of [IrCl(CO)(PPh$_3$)$_2$] with HCl, see: Vaska, L *J. Am. Chem. Soc.* **1966**, *88*, 4100.

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Oxidative Addition of Carboxylic Acid Anhydrides to Rhodium(I) Phosphine Complexes To Produce Novel Rhodium(III) Acyl Derivatives

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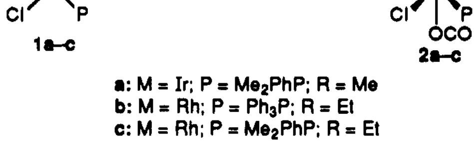
Summary: Oxidative addition of carboxylic acid anhydrides to low-valent Rh(I) phosphine compounds takes place under mild conditions to produce the corresponding Rh(III) acyl complexes, in which the carboxylate ligand is bidentate in nature.

The oxidative addition of acetic anhydride to the Ir(I) complex **1a** has been reported to proceed under mild conditions and produce the respective stable Ir(III) acyl derivative **2a** (eq 1).[2] While a few examples of reactions of Rh(I) compounds with anhydrides have been reported[3a–c] and in one case the corresponding oxidative-addition



1a–c **2a–c** (1)

a: M = Ir; P = Me$_2$PhP; R = Me
b: M = Rh; P = Ph$_3$P; R = Et
c: M = Rh; P = Me$_2$PhP; R = Et

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[2] Blake, D. M.; Shields, S.; Wyman, L. *Inorg. Chem.* **1974**, *13*, 1595.

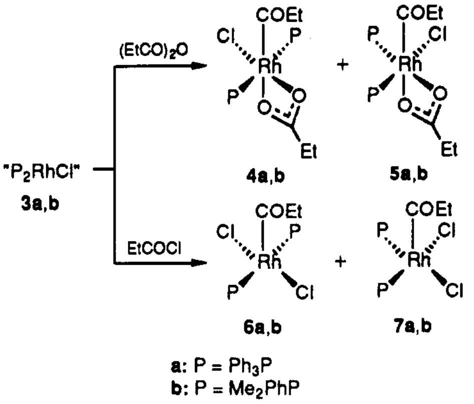
Table I. Analytical Data for Selected Compounds

	anal. calcd (found), %			
compd	C	H	O	P
4a[a]	63.60 (63.97)	5.08 (5.21)	6.05 (6.39)	7.81 (7.91)
6a[a]	62.00 (62.32)	4.67 (4.72)	2.12 (2.44)	8.20 (8.23)
5b	48.49 (48.53)	5.92 (5.98)	8.81 (8.88)	11.37 (11.47)
7b	44.99 (44.89)	5.37 (5.46)	3.15 (3.35)	12.21 (12.11)
9a	50.25 (49.88)	5.94 (5.91)	2.48 (2.88)	14.40 (14.30)

[a] Compounds **4a** and **6a** were dissolved in benzene and then concentrated prior to elemental analysis.

reaction inferred,[3d] the literature is devoid of examples concerning the actual isolation and characterization of such Rh(III) derivatives. Since the facile oxidative addition of acid chlorides to various Rh(I) compounds is well-known,[4] we undertook an investigation of similar reactions with carboxylic acid anhydrides.

Interestingly, attempted reaction of the Rh(I) carbonyl chlorides **1b,c** with propionic anhydride under a variety of conditions yielded no evidence for any formation of the stable acyl adducts **2b,c**, respectively. This is somewhat surprising, as acid chlorides are known to readily oxidatively add to **1c**, and similar alkylphosphine-substituted analogues, under mild reaction conditions.[4a,e,h] We reasoned that use of a low-valent Rh center such as **3a**, which is known to be present in monomeric and/or dimeric form in solutions of Wilkinson's catalyst ($(Ph_3P)_3RhCl \rightleftarrows$ "$(Ph_3P)_2RhCl$" (**3a**) + Ph_3P),[5] might afford a more reactive site for oxidative addition of an anhydride to occur. As anticipated, treatment of a solution of $(Ph_3P)_3RhCl$ with propionic anhydride at 70 °C for 4 h afforded, after recrystallization from methylene chloride–ethyl acetate, the corresponding adduct **4a** as bright orange-yellow crystals in 43% yield (eq 2).[6] The supporting microanalytical data for this new complex, and others, are shown in Table I. The carboxylate ligand of **4a** appears to be bidentate in nature, as evidenced from the IR absorptions assigned to the symmetric and asymmetric (OCOR) frequencies (Table II).[7] Additionally, the trans relationship of the equatorial phosphines in **4a** is clearly indicated by their Rh–P coupling constant of 112.5 Hz found by ^{31}P NMR spectroscopy (Table II), as opposed to 140–150 Hz typically observed for similar complexes possessing the phosphines in a cis orientation.[4n,8] In agreement with previous reports, oxidative addition of propionyl chloride to $(Ph_3P)_3RhCl$ produced the five-coordinate compound **6a**,[4c] again with trans basal phosphine geometry.[9] As shown in Table II, comparison of **4a** with **6a** illustrates their similar spectroscopic behavior.



(2)

Rhodium(I) complexes containing the smaller and more basic Me_2PhP ligands also react with anhydrides to form stable acyl adducts. Thus, sequential treatment of chlorobis(ethylene)rhodium(I) dimer, $[RhCl(C_2H_4)_2]_2$, with Me_2PhP (4 equiv) in toluene to produce **3b**, followed by reaction with excess propionic anhydride at 25 °C for 18 h, afforded, after recrystallization from methylene chloride–ethyl acetate, the Rh(III) acyl complex **5b** as white crystals in 41% yield.[6] Again, both the measurement of J_{Rh-P} in **5b** and comparison with the corresponding adduct **7b** derived from **3b** and propionyl chloride[11] clearly established the cis basal phosphine relationship. As with **4a**, the Me_2PhP-substituted complex **5b** also was evidenced by IR spectroscopy as possessing a bidentate coordinated carboxylate group.

In addition to their decreased steric requirements, the more basic and polarizable Me_2PhP groups might be expected to facilitate oxidative-addition reactions of **3b** relative to the Ph_3P-containing analogue **3a** due to their enhanced ability to lower the promotional energy required for Rh($d^8 \rightarrow d^6$) oxidation. As a consequence, the kinetically formed acyl Rh(III) complexes **5b** and **7b** with cis

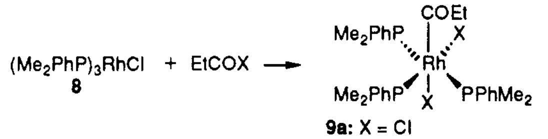
Table II. Spectral Data for Rh(III) Acyl Complexes[a]

				^{13}C NMR[c]				IR[f]		
	^{31}P NMR[c]			acyl					ν_{OCOR}	
complex	δ[d]	J_{Rh-P}[e]	J_{P-P}[e]	δ[d]	J_{Rh-C}[e]	J_{P-C}[e]	δ_{OCOR}[d]	ν_{acyl}	asym	sym
4a	22.18 (d)	112.5		217.8 (dt)	27	6	183.9	1691 (s)	1542 (m)	1461 (m) 1408 (m) 1369 (m)
6a	24.30 (d)	108.5		212.7 (dt)	27	6		1669 (s) 1758 (m)		
4b[b]	22.43 (d)	112.9								
6b[b]	22.34 (d)	112.8								
5b	15.73 (dd) 18.68 (dd)	147.6 143.0	27.7	226.0 (dt)	27	7	187.1	1679 (s)	1541 (m)	1468 (m) 1424 (m) 1369 (w)
7b	17.46 (d)	143.6	27.7	216.1 (dt)	27	7		1675 (s) 1750 (m)		
9a	−4.20 (dd) 9.49 (dt)	104.8 152.1	24.9 24.9	235.4 (dq)	26	5		1641 (s)		
9b[b]	−5.04 (dd) 4.62 (dt)	84.3 112.6	25.4 25.4							

[a] Compounds **4a**, **6a**, **5b**, **7b**, and **9a** all yielded satisfactory analyses for C, H, O, and P (±0.4%). [b] Not isolated. [c] ^{31}P NMR spectra obtained in $CDCl_3$ solvent; ^{13}C NMR spectra obtained in CD_2Cl_2 solvent. [d] Chemical shifts are in ppm with use of 85% H_3PO_4 (^{31}P NMR) or Me_4Si (^{13}C NMR) as reference. Multiplicity is given in parentheses. [e] Coupling constants reported in Hz. [f] KBr pellet (very similar spectra were obtained as Nujol mulls); units are cm^{-1}.

phosphine geometry[12] were isolated from the room-temperature reactions of **3b**, while the higher temperatures utilized for the runs employing $(Ph_3P)_3RhCl$ resulted in the clean formation of the trans isomers **4a** and **6a**. In agreement with this observation is the fact that when **5b** and **7b** were heated in benzene at 70 °C for 2 h, isomerization to the corresponding trans complexes **4b** and **6b** occurred to extents of 7% and 19%, respectively, as judged by ^{31}P NMR spectroscopy (Table II). While it is clear that thermodynamic equilibrium in these instances may not have been reached, the reduced propensity toward isomerization of the complexes **5b** and **7b** containing the smaller Me_2PhP groups (relative to the corresponding Ph_3P-substituted complexes **5a** and **7a**) is, nonetheless, readily apparent.

The oxidative addition of acid chlorides to $(Me_2PhP)_3RhCl$ (**8**)[13] has been previously described and shown to produce the meridional Rh(III) acyl complexes.[4e,p,q] In our hands, for example, treatment of **8** with propionyl chloride in toluene at 25 °C for 1 h selectively produced **9a**[4e,q] in 57% yield, after recrystallization from methylene chloride–ethyl acetate (eq 3). Due to the presence of a highly polarizable phosphine group in place of the π-acidic CO ligand, we anticipated **8** to be more reactive than **1c** toward oxidative addition of an anhydride. Unexpectedly, treatment of **8** with an excess of propionic anhydride in toluene led to the precipitation of a solid product, which was collected and found by ^{31}P NMR spectroscopy to be **9a** (22% yield based on **8**). The filtrate from the same reaction was concentrated and found by ^{31}P NMR methods to consist primarily of three Rh-bound phosphine products identified as **5b**, **7b**, and a compound believed to be either the mono- or bis(propionate) adduct **9b**,[14] in relative amounts of 4.1:1.0:1.1, respectively. These results indicate the occurrence of anion redistribution reactions, a pathway of reaction that is known for some Ir(III) carboxylate derivatives[15] but is apparently without precedent for the corresponding Rh(III) compounds. Futhermore, treatment of the anhydride adduct **5b** with Me_2PhP (1.5 equiv, THF, 25 °C, 2 h) also produced a mixture of redistribution products similar to that obtained directly from the reaction of **8** and propionic anhydride, including **9a,b** and **5b** in relative amounts (by ^{31}P NMR measurements) of 1.3:1.0:7.7, respectively. On the other hand, treatment of **7b** with Me_2PhP under otherwise comparable reaction conditions (THF, 25 °C, 2 h) produced solely the same meridional isomer **9a** (80% yield) as that derived directly from reaction of **8** with propionyl chloride. These experiments illustrate the apparent tendency for Rh(III) acyl complexes possessing a carboxylate ligand to undergo phosphine and/or anion redistribution reactions.



8

9a: X = Cl

b: X = Cl and/or OCOEt

(3)

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. Commercially available solvents ("anhydrous" grade) and reagents were used without further purification.

NMR spectra were recorded on a Varian XL200 advanced NMR instrument. IR spectra were recorded on a Digilab FTS-60 FT-IR spectrometer. Analyses for C, H, and P were performed by Galbraith Laboratories (Knoxville, TN). Oxygen microanalyses were carried out by Leco Corp. (St. Joseph, MI).

Preparation of 4a. A stirred suspension of chlorotris(triphenylphosphine)rhodium(I) (2.00 g, 2.16 mmol) in dry toluene (12 mL) under a nitrogen atmosphere was treated at 25 °C with propionic anhydride (1.12 g, 8.64 mmol). The mixture was heated to 70 °C, stirred for 4 h, and then cooled to room temperature, and to it was added hexane (12 mL). The precipitated solids were collected by filtration, washed with hexane, and then dried in vacuo to yield 1.42 g of crude product as a yellow solid. The product was dissolved in methylene chloride containing a small amount of ethyl acetate, and then this solution was filtered to remove any insolubles. The filtrate was treated with additional

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(6) The yields of crude **4a** and **5b**, precipitated from the corresponding reaction mixture by addition of hexane, were substantially higher (83% and 82%, respectively). ^{31}P NMR spectroscopy showed these crude products to be relatively pure. The possibility of the acyl group in **5b** being instead positioned trans to a phosphine ligand cannot be ruled out from the NMR data presented in Table II. On the basis of the known geometry of analogous acid chloride adducts **7b** and **9a**, however, it seems likely that the relative ligand positions in **5b** are as indicated.

(7) (a) Johnson, B. F. G.; Johnston, R. D.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1971**, 689. (b) Smith, S. A.; Blake, D. M.; Kubota, M. *Inorg. Chem.* **1972**, *11*, 660. (c) Mitchell, R. W.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 3224. (d) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912.

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(9) Although one report has unexpectedly described a five-coordinate Rh(III) acyl complex as possessing trigonal-bipyramidal geometry,[4m] several studies have unequivocally determined a square-pyramidal configuration for a variety of five-coordinate Rh(III) complexes,[4r] including acyl derivatives.[4n,p,q,10]

(10) Moloy, K. G.; Wegman, R. W. *Organometallics* **1989**, *8*, 2883.

(11) Compound **7b** (58% yield as bright yellow crystals) was prepared from $[RhCl(C_2H_4)_2]_2$, Me_2PhP, and propionyl chloride (toluene, 25 °C, 1 h) in a procedure similar to that used for **5b**. The oxidative addition of acetyl chloride to "$(Me_2PhP)_2RhCl$" has been reported previously to produce an apparent isomeric mixture of the corresponding five-coordinate Rh(III) acyl complex.[4p]

(12) The oxidative addition of acetyl chloride to **3a** has previously been demonstrated to produce initially the adduct of cis basal phosphine geometry, which subsequently isomerizes to the corresponding trans complex.[4c,n]

(13) Intille, G. M. *Inorg. Chem.* **1972**, *11*, 695.

(14) The ^{31}P NMR data (Table II) are consistent with that expected for **9b** and, as might be predicted, are fairly similar to those found for **9a**.

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ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.55 g (58%) of **4a** as bright yellow crystals, mp 200–204 °C dec. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.02 (t, 3 H), 0.09 (t, 3 H), 0.74 (q, 2 H), 2.16 (q, 2 H), 7.3–7.5 (m, 18 H), 7.6–7.8 (m, 12 H).

Preparation of 6a. A stirred suspension of chlorotris(triphenylphosphine)rhodium(I) (2.00 g, 2.16 mmol) in dry toluene (15 mL) under a nitrogen atmosphere was treated at 25 °C with propionyl chloride (0.30 g, 3.24 mmol). The mixture was heated to 70 °C, stirred for 1 h, and then cooled to room temperature, and to it was added hexane (15 mL). The precipitated solids were collected by filtration, washed with hexane, and then dried in vacuo to yield the crude product as an orange-red solid. The product was dissolved in methylene chloride containing a small amount of ethyl acetate, and then this solution was filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.31 g (80%) of **6a** as orange-red crystals, mp 200–204 °C dec. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.78 (t, 3 H), 2.94 (q, 2 H), 7.3–7.5 (m, 18 H), 7.6–7.8 (m, 12 H).

Preparation of 5b. To a stirred suspension of chlorobis(ethylene)rhodium(I) dimer (1.00 g, 2.62 mmol) in dry toluene under a nitrogen atmosphere was added at 25 °C dimethylphenylphosphine (1.45 g, 10.5 mmol). The resultant dark solution was stirred at room temperature for 30 min and then was treated with propionic anhydride (1.02 g, 7.86 mmol). The reaction mixture was stirred at room temperature for 18 h, and then to it was added hexane (15 mL). The precipitated solids were collected by filtration, washed with hexane, and then dried in vacuo to yield 2.34 g of the crude product as an off-white solid. The product was dissolved in methylene chloride containing a small amount of ethyl acetate and then filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.18 g (41%) of **5b** as white crystals, mp 144–145 °C dec. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.09 (t, 3 H), 1.16 (t, 3 H), 1.35 (broad d, 6 H), 1.73 (broad m, 6 H), 2.32 (q, 2 H), 3.44 (m, 2 H), 7.1–7.27 (m, 4 H), 7.28–7.5 (m, 6 H).

Preparation of 7b. To a stirred suspension of chlorobis(ethylene)rhodium(I) dimer (1.00 g, 2.62 mmol) in dry toluene (15 mL) under a nitrogen atmosphere was added at 25 °C dimethylphenylphosphine (1.45 g, 10.5 mmol). The resultant dark solution was stirred at room temperature for 30 min and then was treated with propionyl chloride (0.61 g, 6.55 mmol). The reaction mixture was stirred at room temperature for 1 h, and then to it was added hexane (15 mL). The precipitated solids were collected by filtration, washed with hexane, and then dried in vacuo to yield 2.50 g of the crude product as a yellow powder. The product was dissolved in methylene chloride containing a small amount of ethyl acetate, and then this solution was filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.55 g (58%) of **7b** as bright yellow crystals, mp 145–148 °C dec. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.14 (t, 3 H), 1.33 (d, 6 H), 1.81 (d, 6 H), 3.86 (t, 2 H), 7.2–7.6 (m, 10 H).

Preparation of 9a. To a stirred suspension of chlorobis(ethylene)rhodium(I) dimer (0.75 g, 1.96 mmol) in dry toluene (15 mL) under a nitrogen atmosphere was added at 25 °C dimethylphenylphosphine (1.89 g, 13.8 mmol). The resultant dark solution was stirred at room temperature for 30 min and then was treated with propionyl chloride (0.73 g, 7.86 mmol). The reaction mixture was stirred at room temperature for 1 h, and then to it was added hexane (15 mL). The supernatant liquid was decanted from the solid, which was then washed with hexane and dried in vacuo. The product was dissolved in methylene chloride containing a small amount of ethyl acetate and then filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.45 g (57%) of **9a** as yellow crystals, mp 150–154 °C dec. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.67 (t, 3 H), 1.27 (d, 6 H), 1.86 (m, 12 H), 2.79 (q, 2 H), 7.2–7.5 (m, 15 H).

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Reaction of Cationic Diiron μ-η^1:η^2-Acetylide Complexes $[(FP)_2(C{\equiv}CR)]BF_4$ (R = H, Ph) with Carbon Nucleophiles and Hydride. Formation of μ-Vinylidene Complexes

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Summary: The reaction of a cationic diiron μ-η^1:η^2-acetylide complex $[(FP)_2(C{\equiv}CH)]BF_4$ (**1**) with RLi (R = *n*-Bu, *t*-Bu) affords an acyl-substituted vinylidene complex $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}CH(COR)]$ (**3a**, R = *n*-Bu; **3b**, R = *t*-Bu). The structure of **3b** has been determined by single-crystal X-ray diffraction study. [Crystal data for **3b**: space group $P2_1/c$, a = 17.460 (2) Å, b = 9.495 (2) Å, c = 17.446 (2) Å, β = 100.480 (9)°, V = 2843.8 (7) Å^3, Z = 4, R = 0.0822.] **3** may be formed by an initial nucleophilic attack of R$^-$ to a CO ligand in the cationic Fp* part, followed by insertion of the C≡C part into the Fe–C(O)R bond and metal–metal bond formation. The reaction of **1** with $LiHBEt_3$ affords a parent μ-vinylidene complex $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (**4**). A plausible reaction pathway involves nucleophilic addition of H$^-$ to a CO ligand and successive intramolecular hydride transfer from the formyl ligand to the β position of the C≡CH ligand.

The reactivity of $CpFe^+(CO)(L)(\eta^2\text{-alkyne})$ complexes [L = PR_3, $P(OR)_3$] toward nucleophiles has been extensively studied by Reger et al.[1] Most nucleophiles attack the coordinated η^2-alkyne ligand from the exo side to give trans-η^1-alkenyl ligands, which have been successively derivatized to functionalized alkenes (Scheme I). Exceptions are H$^-$,[2] R_2N^-,[3] and RLi,[3] which add to the Cp ring, and subsequent intramolecular hydride transfer from the transient η^4-C_5H_5–Nu ligand to the η^2-alkyne ligand results in the formation of cis-η^1-alkenyl ligands.

We have been studying the reactivity of cationic diiron μ-η^1:η^2-acetylide complexes $[(FP)_2(C{\equiv}CR)]BF_4$ [**1**, FP = Fp*, R = H; **2a**, FP = Fp*, R = Ph; **2b**, FP = Fp, R = Ph; FP = $(CP)Fe(CO)_2$, CP = η^5-$C_5R'_5$; Cp, Fp (R′ = H); Cp*,

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