One-Electron Oxidation of Heterodinuclear Organometallic Compounds Having Polyphosphido Bridges[†]

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The electrochemical behavior of several heterometallic compounds having polyphosphido bridges has been investigated. Reversible one-electron oxidations were observed for $\text{Cp}^*\text{Fe}(\text{P}_5)\text{TaCp}''$ (**2**), $\text{Cp}^*\text{Fe}(\text{P}_5)[\text{Ir}_2(\text{CO})_2\text{Cp}^*_2]$ (**3**), and $\text{Cp}'''\text{Co}_2(\text{P}_2)_2$ (**4**) ($\text{Cp}^* = \text{C}_5\text{M}_5$, $\text{Cp}'' = \text{C}_5\text{H}_3^t\text{Bu}_2$, $\text{Cp}''' = \text{C}_5\text{H}_2^t\text{Bu}_3$). In contrast to the pseudo-sandwich polyphosphido complex Cp^*FeP_5 (**1**), compounds **2–4** undergo very facile oxidations and the corresponding monocations may be generated by bulk electrolysis or by reaction with ferrocenium ion. $E_{1/2}$ values (vs $\text{Cp}_2\text{Fe}^{0/+}$) for the oxidations are -0.24 V for **2**, -0.58 V for **3**, and -0.33 V for **4** in $\text{CH}_2\text{Cl}_2/0.1$ M $[\text{NBu}_4][\text{PF}_6]$, in contrast to 0.57 V for **1**. Although ESR spectra of **2**⁺ display hyperfine coupling to ^{181}Ta , the SOMO appears to have only minor Ta character. IR spectroelectrochemistry of the **3/3**⁺ couple reveals an increase of ν_{CO} of only 11 cm^{-1} , indicating that the oxidation of **3** also occurs predominantly at the iron center. The fact that the Fe-based oxidations of **2** and **3** are more negative than that of **1** by ca. 0.8 and 1.15 V, respectively, is ascribed to differences in the iron formal oxidation state which arise from the structural variations of the P_5 bridging groups.

Introduction

Within the context of ongoing research in heterodinuclear polyorganometallic chemistry,^{1–8} compounds containing polyphosphido bridges have drawn some attention owing to the variety of structural and bridging modes possible with these ligands.⁹ Some electrochemical studies have been reported on sandwich compounds containing the cyclopentadienyl-like pentaphosphacyclopentadienyl (P_5) or hexaphosphabenzene (P_6) ligand, such as Cp^*FeP_5 ¹⁰ (**1**) and $\text{Cp}^*\text{M}_2(\text{P}_6)$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$,

V).¹¹ Because the electronic structures of the latter are similar to that of a triple-decker complex, they show electrochemical behavior typical of a highly delocalized multi-metallic system.¹¹ Very little has appeared^{8,9b} on the redox properties of multinuclear complexes having phosphido bridges which are not Cp analogues. We now report electrochemical results on two structurally characterized¹² compounds having Cp^*Fe linked to either a monometallic or dimetallic moiety through a more irregular P_5 ligand. In $\text{Cp}^*\text{Fe}(\text{P}_5)\text{TaCp}''$ (**2**),¹³ one of the P–P bonds of the P_5 group is broken and the 18-electron configuration is achieved for both metals by the formation of an Fe–Ta bond. Although the P_5 system remains cyclic in $\text{Cp}^*\text{Fe}(\text{P}_5)[\text{Ir}_2(\text{CO})_2\text{Cp}^*_2]$ (**3**), it is no longer planar. In this case a metal–metal bond is not needed to achieve an 18-electron configuration for Fe.¹²

As will be shown below, the one-electron oxidations of **2** and **3** are surprisingly facile, with $E_{1/2}$ values that are 0.80 and 1.15 V more negative, respectively, than the value of 0.57 V vs $\text{Cp}_2\text{Fe}^{0/+}$ measured for **1**^{0/+}.¹⁰ Spectroscopic measurements (ESR, IR) indicate that, despite the contrasting $E_{1/2}$ values, the oxidations are localized primarily on the Cp^*Fe moiety. The dicobalt complex $\text{Cp}'''\text{Co}_2(\text{P}_2)_2$ (**4**) was also investigated, although in less detail since some electrochemistry had been reported earlier on the closely related complex $\text{Cp}^*\text{Co}_2(\text{P}_2)_2$.^{8b}

[†] Dedicated to Prof. Otto J. Scherer of University of Kaiserslautern on his becoming emeritus.

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(1) Gates, B. C. *Chem. Rev.* **1995**, *95*, 511.

(2) Ichikawa, M. *Adv. Catal.* **1992**, *38*, 283.

(3) Aubart, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1793.

(4) Nashner, M. S.; Somerville, D. M.; Lane, P. D.; Alder, D. L.; Shapley, J. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 12964.

(5) Mukerjee, S.; Srinivasan, S.; Soriaga, M. P.; McBreen, J. J. *Electrochem. Soc.* **1995**, *142*, 1409.

(6) (a) Lemoine, P. *Coord. Chem. Rev.* **1988**, *83*, 169. (b) Zanello, P. *Coord. Chem. Rev.* **1988**, *83*, 169. (c) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87.

(7) Collins, B. Y.; Koide, Y.; Schauer, C. K.; White, P. S. *Inorg. Chem.* **1997**, *36*, 6172.

(8) (a) Barr, M. E.; Adams, B. R.; Weller, R. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 3052. (b) Barr, M. E.; Dahl, L. F. *Organometallics* **1991**, *10*, 3991.

(9) See, for example: (a) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924. (b) Scheer, M. Z. *Chem.* **1990**, *29*, 41. (c) Barr, M. E.; Adams, B. R.; Weller, R. R.; Dahl, L. E. *J. Am. Chem. Soc.* **1991**, *113*, 3052. (d) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1004. (e) Scherer, O. J. *Acc. Chem. Res.* **1999**, *32*, 751. (f) Ehses, M.; Romero, A.; Peruzzini, M. *Top. Curr. Chem.* **2002**, *220*, 107.

(10) Winter, R. F.; Geiger, W. E. *Organometallics* **1999**, *18*, 1827 and references therein.

(11) Scherer, O. J.; Schwalb, J.; Swarowsky, H.; Kaim, W.; Gross, R. *Chem. Ber.* **1988**, *121*, 443.

(12) Compounds **2** and **3**: Detzl, M.; Mohr, T.; Scherer, O. J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1110. Compound **4**: Scherer, O. J.; Berg, G.; Wolmershäuser, G. *Chem. Ber.* **1995**, *128*, 635.

(13) $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3^t\text{Bu}_2$ -1,3, $\text{Cp}''' = \eta^5\text{-C}_5\text{H}_2^t\text{Bu}_3$ -1,2,4.

Experimental Section

All experiments were conducted under an atmosphere of dinitrogen using standard Schlenk and drybox procedures. Solvents were dried and distilled before use. Electrochemical procedures were carried out using solvents that had been vacuum-distilled into flasks that were then transferred to the drybox. Compounds **2**–**4**¹² were provided by the Scherer group.

Electrochemical experiments were conducted in either CH_2Cl_2 or THF. The former was distilled from calcium hydride, and the latter was subjected to successive distillations from CaH_2 , potassium, and (deep purple) K/benzophenone. The supporting electrolyte was 0.1 M $[\text{NBu}_4][\text{PF}_6]$. The experimental reference electrode was a Ag/AgCl electrode prepared by anodizing a silver wire in an HCl solution. Ferrocene was added as an internal standard at an appropriate point in the experiment, and all potentials in this paper are referenced to $\text{Cp}_2\text{Fe}^{0/+}$.¹⁴ Voltammetric measurements were performed using a PARC Model 173 potentiostat interfaced to home-written software. Solution temperatures were controlled to better than 1 °C precision. Infrared thin-layer spectroelectrochemistry (IRTLE) experiments were conducted as described earlier.¹⁵ Voltammetric diagnostics followed the procedures previously noted,¹⁶ expanded experimental details may be obtained from ref 10.

Table 1. Electrochemical Potentials (vs $\text{Cp}_2\text{Fe}^{0/+}$) of Selected Polyphosphido Complexes in Nonaqueous Solvents Containing 0.1 M $[\text{NBu}_4][\text{PF}_6]$

compd	solvent	oxidn		redn
		0/1+	oxdn of 1+	
Cp*Fe(P ₃)TaCp'' (2)	CH ₂ Cl ₂	-0.24	ca. 1 ^a	-2.58 ^b
2	THF	-0.14	not measd	-2.56 ^c
Cp*Fe(P ₃)[Ir ₂ (CO) ₂ Cp* ₂] (3)	CH ₂ Cl ₂	-0.58	0.25 ^d	not measd
Cp'' ₂ Co ₂ (P ₂) ₂ (4)	CH ₂ Cl ₂	-0.33	0.33	
Cp* ₂ Co ₂ (P ₂) ₂ (5)	CH ₃ CN	-0.16 ^e	0.15 ^{e,f}	
Cp*FeP ₅ (1)	CH ₂ Cl ₂	0.57 ^g		-2.00 ^h

^a Broad, ill-defined multielectron wave. ^b Irreversible wave close to solvent background. ^c E_{pc} at scan rate = 0.1 V/s; irreversible wave of two-electron height. ^d E_{pa} at scan rate = 0.1 V/s; see text for more details. ^e Reference 8b. ^f Chemically irreversible one-electron process. ^g Reference 10.

Figure 1. Cyclic voltammogram of 0.5 mM **2** in CH₂Cl₂/0.1 M [NBu₄][PF₆] at a glassy-carbon electrode (2 mm diameter) at ambient temperature and a scan rate of 0.1 V/s.

Results

In $\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{PF}_6]$, compounds **2–4** each undergo an essentially reversible one-electron oxidation to the corresponding monocation, followed by a further one-electron oxidation which varies in its chemical reversibility. In addition, irreversible reductions of compounds **2** and **3** were observed in THF; since the cathodic processes gave a number of electroactive products, they were not studied in detail.

Table 1 gives the measured $E_{1/2}$ and E_{peak} potentials vs ferrocene/ferrocenium for these compounds and for the monometallic analogue **1**.

The oxidation of **2** (Figure 1) was shown to be a chemically and electrochemically reversible, diffusion-controlled, one-electron process ($E_{1/2} = -0.24$ V in $\text{CH}_2\text{-Cl}_2$, -0.14 V in THF). The diffusion coefficients, D , measured by chronoamperometry with 4 s step times,¹⁷ were 1.0×10^{-5} cm²/s in THF/0.15 M $[\text{NBu}_4][\text{PF}_6]$ at 300 K and 5.6×10^{-6} cm²/s at 271 K. The chemical reversibility of the couple was confirmed by cyclic voltammetry (CV, scan rates of 0.05 to 0.5 V/s) and double-potential step chronoamperometry (1–4 s step times) at room temperature. The essentially Nernstian nature of **2/2**⁺ was indicated by the fact that the ΔE_p values in CV scans were very close to those observed for ferrocene under the same conditions (typically 70 mV at $v = 0.05$ V/s).

(17) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001; pp 207–210.

(14) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

(15) Atwood, C. G.; Geiger, W. E.; Bitterwolf, T. E. *J. Electroanal. Chem.* **1995**, 397, 279.

(16) Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; p. 683 ff.

Exhaustive bulk oxidation of **2** at 276 K in $\text{CH}_2\text{Cl}_2/0.1 \text{ M} [\text{NBu}_4][\text{PF}_6]$ ($E_{\text{appl}} = 0.2 \text{ V}$) released 1.2 faradays/equiv as the solution went from an olive green to a dark red-brown. Comparison of rotating-Pt-electrode scans before and after electrolysis suggested the efficient production of the monocation **2**⁺. After a period of about 40 min, a back-electrolysis was carried out at $E_{\text{appl}} = -0.6 \text{ V}$, requiring 1.1 faradays/equiv and regenerating an essentially quantitative amount of neutral **2**. When this “forward and backward” electrolysis was repeated, a small amount (<5%) of a secondary product was formed which had an oxidation wave of modest chemical reversibility at $E_{1/2} = 0.57 \text{ V}$, identical with that of **1**. The presence of **1** as a side product was confirmed by addition of a genuine sample of Cp^*FeP_5 , which enhanced the current of the secondary product wave. The long-term oxidation process of **2** is as described in eq 1.

Attempts to isolate X-ray-quality crystals of **2**⁺ were unsuccessful. Chemical oxidation of **2** by 1 equiv of $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ in CH_2Cl_2 produced only orange-brown microcrystals after 3 days at 240 K. When this experiment was repeated in CD_2Cl_2 , it was found by NMR spectroscopy that **2**⁺ was undergoing slow decay to neutral **2** with some **1** also present. It was possible, however, to obtain ESR spectra of **2**⁺ generated either by the bulk coulometric oxidations described above or by a chemical oxidation using $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ in 1:1 $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$. Fluid-solution spectra were recorded over the temperature range of 190–240 K, with increased resolution being obtained at higher temperatures. The spectra are consistent with the presence of an eight-line hyperfine splitting from the Ta nucleus: $\langle a \rangle = 42 \text{ G}$ and $\langle g \rangle = 2.0940$ (Figure 2a) (^{181}Ta , 99.99%, $I = 7/2$). The frozen-solution spectra were much more complex, with highly overlapped sets of apparent octets of hyperfine lines (Figure 2b). It appears that A_{Ta} is approximately 45–50 G for two of the three principal directions, and in conjunction with the measured isotropic value of 42 G, a third A_{Ta} value of 25–35 G is estimated. Using the measured and estimated hyperfine values and assuming approximate axial symmetry, one calculates less than 1% Ta 6s character and 5–15% Ta 3d character for the SOMO of **2**⁺.¹⁸ The dominant metal character in this radical appears to be at the ESR-silent Fe atom.

When the more strongly donating solvent THF was used in bulk anodic electrolyses of **2**, several electroactive decomposition products were observed, the main

Figure 2. X-band ESR spectra of **2**⁺ in 1:1 $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$: (a) fluid-solution spectrum at 240 K; (b) frozen spectrum at 77 K. The position of the DPPH standard is indicated.

oxidation product being mononuclear **1** ($T = 276 \text{ K}$, dark green solution, 3 faradays/equiv).

The trinuclear FeIr_2 complex **3** undergoes two sequential one-electron oxidations at potentials of $E_{1/2} = -0.58 \text{ V}$ and $E_p = 0.25 \text{ V}$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M} [\text{NBu}_4][\text{PF}_6]$. The first of these, assigned to the couple **3**^{+/3}⁺, is highly reversible, whereas the second, assigned to **3**^{+/3}²⁺, has the anodic shape of a slow electron-transfer process¹⁹ with a cathodic return feature suggestive of electrode product adsorption. The overall chemical reversibility of the **3**/**3**⁺ couple was investigated by bulk electrolysis of **3** at 265 K ($E_{\text{appl}} = -0.3 \text{ V}$, 1.1 faradays/equiv, dark green color). Small waves arising from compound **1** were seen, indicating the slow decomposition of **3**⁺. Back-electrolysis ($E_{\text{appl}} = -0.9 \text{ V}$, 0.56 faradays/equiv) led to 50% regeneration of the starting material, **3**. From this experiment and from the time dependence of EPR intensities of solutions of **3**⁺, the half-life of the radical cation is estimated as about 1 h. The anodic electrolysis solution containing **3**⁺ had a frozen-solution ESR spectrum of rhombic character with $g_1 = 2.2044$, $g_2 = 2.0483$, and $g_3 = 1.9981$. The average g value of 2.0836 is consistent with the measured fluid solution spectrum, which has $g = 2.0820$, with a peak-to-peak width of 20 G at 250 K. No hyperfine splittings were observed in either glassy or fluid solutions. Identical ESR results were obtained by treating $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$ solutions of **3** with $[\text{Cp}_2\text{Fe}][\text{BF}_4]$. The ESR spectra are reminiscent of those seen previously¹⁰ for **1**⁺ (2.1961, 2.1095, 2.0071 (average 2.104)) and are consistent with a predominantly iron-based spin localization in **3**⁺.

(18) Using a model of axial symmetry, one can estimate the fraction of s vs p and d character on the Ta nucleus. Since the maximum isotropic hyperfine splitting for ^{181}Ta is 5360 G, the measured value of $\langle a \rangle = 42 \text{ G}$ gives 0.78% for the 6s radical character. Using the estimated values of $A_{\text{Ta}}(1) = A_{\text{Ta}}(2) = 45\text{--}50 \text{ G}$ and $A_{\text{Ta}}(3) = 25\text{--}35 \text{ G}$, along with a uniaxial theoretical hyperfine constant of 64 G for ^{181}Ta , one obtains a scatter of 5–15% tantalum 5d character. For details of this treatment see: Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*, Wiley: New York, 1994; Chapters 5 and 9 and Table G.4.

(19) The anodic peak at $E_p = 0.25 \text{ V}$ has a breadth of $E_{\text{pa}} - E_{\text{pa}/2}$ of 105 mV at $\nu = 0.1 \text{ V s}^{-1}$, much larger than that (ca. 60 mV) expected for a reversible system under these conditions. The anodic peak current is only about 80% of that for the couple **3**/**3**⁺, once again in keeping with the electrochemically irreversible nature of **3**^{+/3}²⁺. See ref 17, pp 234–243.

Figure 3. ν_{CO} spectral changes upon IRTTLE oxidation of 2 mM **3** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{NBu}_4][\text{PF}_6]$. As the oxidation proceeds, the absorption of **3** (ν_{CO} 1953 cm^{-1}) is replaced by that of **3**⁺ (ν_{CO} 1964 cm^{-1}).

Figure 4. Cyclic voltammogram of 0.5 mM **4** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{NBu}_4][\text{PF}_6]$ at a glassy-carbon electrode (2 mm diameter), at $T = 250 \text{ K}$ and a scan rate 0.1 of V/s. The small feature at $E_{\text{pa}} = 0.65 \text{ V}$ arises from the decomposition of **4**²⁺.

When a portion of the anodic electrolysis solution containing **3**⁺ was removed for an IR analysis, a band at ν 1964 cm^{-1} was observed, shifted only 11 cm^{-1} from ν 1953 cm^{-1} for the neutral complex **3**. Since a small band was also observed at ν 2037 cm^{-1} , an IR-transparent thin-layer electrochemistry (IRTTLTLE) experiment¹⁵ was undertaken to clarify the assignments. In this case, electrolysis of **3** at $E_{\text{appl}} = 0.1 \text{ V}$ resulted in smooth conversion of **3** (ν_{CO} 1953 cm^{-1}) to **3**⁺ (ν_{CO} 1964 cm^{-1}) without production of IR-active side products (Figure 3). Back-reduction of **3**⁺ regenerated over 80% of the original spectrum of **3**. The very small increase in ν_{CO} upon one-electron oxidation of **3** is strongly suggestive that the positive charge in **3**⁺ lies predominantly with Fe, rather than at the Ir atoms.

The dicobalt complex **4** displays two one-electron-oxidation processes. The first of these, involving **4**/**4**⁺ ($E_{1/2} = -0.33 \text{ V}$) is essentially Nernstian, with a diffusion coefficient of $5.7 \times 10^{-6} \text{ cm}^2/\text{s}$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{NBu}_4][\text{PF}_6]$ at 296 K. A second one-electron oxidation to **4**²⁺ ($E_{1/2} = 0.33 \text{ V}$) has limited chemical reversibility at room temperature but is more reversible at 250 K

(Figure 4). Electrochemical measurements for the very similar complex $\text{Cp}^*\text{Co}_2(\text{P}_2)_2$ (**5**) concluded that it is reversibly oxidized to **5**⁺ at -0.16 V , followed by an irreversible second oxidation at 0.15 V.^{8b} The present result for the **4**/**4**⁺ couple is consistent with the earlier finding for **5**/**5**⁺, except for our measurement of a significantly larger separation between the first and second oxidations of **4** (ca. 660 mV) than the value of ca. 330 mV estimated^{8b} for **5**.

Bulk oxidation of **4** in CH_2Cl_2 at $E_{\text{appl}} = 0 \text{ V}$ resulted in the clean conversion to **4**⁺ (250 K, 1.03 faradays/equiv, change of color from brown of **4** to yellow-green of **4**⁺), and reverse electrolysis at $E_{\text{appl}} = -0.6 \text{ V}$ gave back the starting material **4** in 95% yield. The oxidized solution gave a glassy ESR spectrum with a broad (200 G) resonance having the appearance of an approximately axially symmetric *g* tensor with $g_{\parallel}$ and $g_{\perp}$ close to 2.03. No hyperfine splittings were observed. When the generation of **4**⁺ was repeated using $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ as an oxidant, a fluid-solution spectrum was observed, but again the lines were too broad to allow assignment of hyperfine splittings.

Discussion

Two significant points about the one-electron oxidations of **2** and **3** are that (i) they occur at $E_{1/2}$ values that are strongly negative of $E_{1/2}$ for the oxidation of **1** and (ii) the spectral (ESR and IR) properties of **2**⁺ and **3**⁺ show that the oxidations of both **2** and **3** are essentially iron-based.

Strong evidence for this conclusion is the fact that ν_{CO} increases by only 11 cm^{-1} in going from $\text{Cp}^*\text{Fe}(\text{P}_5)[\text{Ir}_2(\text{CO})_2\text{Cp}^*_2]$ to $[\text{Cp}^*\text{Fe}(\text{P}_5)\{\text{Ir}_2(\text{CO})_2\text{Cp}^*_2\}]^+$, whereas a much larger increase would be expected if the HOMO of **3** is primarily localized on the diiridium site. According to previous literature,²⁰ the oxidation of trinuclear metal-carbonyl clusters having delocalization over all three metals results in ν_{CO} increases of 60–80 cm^{-1} . The simplest interpretation of the IR spectrum of **3**⁺ is that the effect of oxidation at the iron center is transmitted through the σ framework to the Ir_2 center as an inductive effect.

A similar conclusion, namely that the spin distribution is minimally on the non-iron metal, is reached in evaluating the ESR spectra of **2**⁺. The hyperfine splitting from ¹⁸¹Ta is prominent because this nucleus has a rather large nuclear *g* factor.²¹ The lack of a fully resolved glassy spectrum of **2**⁺ (Figure 2), along with the possible role of quadrupole effects such as those found in other third-row-metal radicals,²² precludes an analysis of the Ta hyperfine splittings sufficient to give a detailed orbital assignment.

However, using reasonable approximations,¹⁸ we conclude that there is a spin density on Ta of ca. 10%. Although there is not a broad literature of ESR spectra of heterodinuclear radicals having M–M' bonds, there has been a spectrum reported for the Ta–Co radical, $\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{CoCp}$.²³ In that case, despite the demon-

(20) Robben, M. P.; Rieger, P. H.; Geiger, W. E. *J. Am. Chem. Soc.* **1999**, *121*, 367.

(21) See: Weil, J. A. et al. In ref 18, p 536.

(22) Connelly, N. G.; Emslie, D. J. H.; Klangsinirikul, P.; Rieger, P. H. *J. Phys. Chem. A* **2002**, *106*, 51.

(23) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4853.

strated presence of a Ta–Co bond, the glassy spectrum showed a hyperfine interaction with only one of the metals. Since both metals have $I = 7/2$, an indirect assignment of the splitting was required, with the authors favoring an assignment to Ta rationalized on a preferred Co(III)/Ta(IV) electronic structure. A similar line of reasoning would suggest an assignment of Fe(II)/Ta(IV) in **2**⁺ (vide infra). Although this is surely an oversimplification of the electronic structure of the Fe–Ta cation, it accentuates the point that a Ta-based oxidation of **2** is not necessary to account for the ESR properties of **2**⁺.

Finally, the ease of oxidation of **2** and **3** deserves comment, since the negative shifts compared to **1** (800 and 1150 mV, respectively) seem too large to be accounted for by simple inductive effects. Rather, the ease of oxidation is ascribed to changes in the formal oxidation state of the iron atom concomitant with changes in the bonding mode of the P₅ ligand upon addition of one or two more transition metals for **2** and **3**, respectively. For **1** itself, the bonding closely resembles that of ferrocene with an Fe(II) coordinated to Cp*[−] and P₅[−] rings. In contrast, the P₅ unit in **2** is best described as an open chain pentaphosphapenta-1,4-dienetriide (P₅^{3−}), following a formalism that assigns every two-coordinated phosphorus atom either a negative or a positive charge.²⁴ The iron atom is coordinated to two P=P bonds and to the pentamethylcyclopentadienide, while the

tantalum atom forms bonds to another substituted cyclopentadienide and the three negatively charged terminal and central phosphorus atoms of the P₅ chain. The resulting formal oxidation states of iron and tantalum are +I and +IV, respectively.

In complex **3** the Fe atom is in essentially the same bonding environment as in **2**, with the exception of the absence of an Fe–metal bond. The diamagnetism of this compound and the 18-electron rule suggest at least a partial contribution from a zwitterionic electronic structure involving a negatively charged Fe(0) atom counterbalanced by a positive charge on the central P atom of the cyclo-P₅ ring. In this way a PR₂⁺ unit contributes two valence electrons to the diiridium entity. The moiety [{Cp*(CO)Ir}₂(μ-PR₂)]⁺ thus achieves a 34-electron count, in agreement with the observed iridium–iridium bond. The $E_{1/2}$ values of the oxidations of compounds **1–3** are therefore seen to parallel a decrease in the formal Fe oxidation state and are consistent with ESR and IR spectroscopic results which place the SOMO primarily on the Fe center in the cations of all three compounds.

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(24) von Schnering, H. G.; Hönlé, W. *Chem. Rev.* **1988**, *88*, 243.