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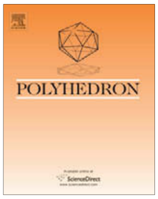

New rhenium(I) compounds containing the donor–acceptor diphosphine ligands 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)4-cyclopenten-1,3-dione (fbpcd) and 2-(3-ferrocenylprop-2-ynylidene)-4,5-bis(diphenylphosphino)4-cyclopenten-1,3-dione (fpbpcd): Electrochemical behavior, MO properties, and X-ray diffraction structure of *fac*-BrRe(CO)$_3$(fpbpcd)

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A R T I C L E I N F O

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A B S T R A C T

Displacement of the labile THF molecules in BrRe(CO)$_3$(THF)$_2$ (**1**) by the diphosphine ligands 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)4-cyclopenten-1,3-dione (fbpcd) and 2-(3-ferrocenylprop-2-ynylidene)-4,5-bis(diphenylphosphino)4-cyclopenten-1,3-dione (fpbpcd) yields the mononuclear compounds *fac*-BrRe(CO)$_3$(fbpcd) (**2**) and *fac*-BrRe(CO)$_3$(fpbpcd) (**3**), respectively. The new ligand fpbpcd ligand has been synthesized from 3-ferrocenylpropynal and the parent diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) through a Knoevenagel condensation. **2** and **3** have been isolated and fully characterized by IR and NMR spectroscopies (^{1}H and ^{31}P), ESI mass spectrometry, and X-ray diffraction analysis in the case of **3**. The electrochemical properties of compounds **2** and **3** have been examined by cyclic voltammetry, and the nature of the HOMO and LUMO levels in these systems has been confirmed by MO calculations at the extended Hückel level. The redox and MO data are discussed relative to the redox and orbital properties of related functionalized diphosphines based on the bpcd platform.

1. Introduction

New inorganic and organometallic systems that can promote energy- and electron-transfer reactions are highly sought after as device components in optoelectronic applications, photosynthetic mimics, redox switches, and model systems for directional charge-transfer processes [1]. The synthesis and photophysical study of new luminescent organometallic complexes continue to command the attention of a diverse group of researchers. Many dyad and triad arrays possessing an energetically accessible LUMO typically give rise to long-lived charge-transfer species, a condition tantamount for the successful fabrication of photosynthetic and OLED devices [2]. While many derivatives exhibit a low-lying LUMO and promote long-lived charge separated species, the search for new systems with tunable LUMO levels remains a universal priority.

While diphosphine ligands are ubiquitous in transition-metal chemistry, only a few documented paradigms exist that display significant luminescent behavior [3]. Undoubtedly, the principal factor responsible for the disappointing photophysical data (i.e., efficient non-radiative decay) experimentally found in the overwhelming majority of diphosphine-substituted metal compounds is the absence of a low-lying π^* acceptor LUMO on the diphosphine ligand. The absence of an energetically accessible diphosphine LUMO radically changes the emissive behavior relative to those compounds containing an α-diimine or related heterocyclic ligand that possess a π^* LUMO that is localized on the ancillary heterocyclic residue [4].

Our groups maintain a longstanding interest in the synthesis and physical study of organometallic complexes containing the unsaturated diphosphine ligands 2,3-bis(diphenylphosphino) maleic anhydride (bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) [5,6]. These particular ligands are unique vis-á-vis the common diphosphine ligands dppm, (Z)-1,2-$Ph_2PCH{=}CHPPh_2$, and 1,2-bis(diphenylphosphino)benzene because both bma and bpcd exhibit a one-electron reduction at relatively low potential (<−1.1 V), with electron accession occurring at a π^*-based LUMO that is localized about the central platform ring [7]. The superb electron reservoir properties displayed by bma and bpcd have been shown to modulate ligand substitution in selected mononuclear compounds having electron counts in excess of 18e- [8].

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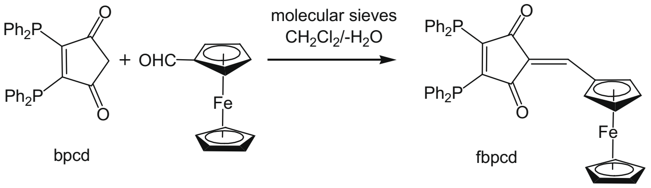
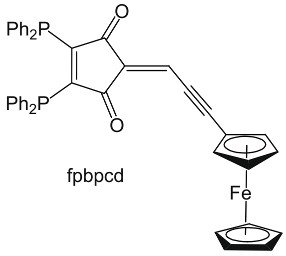
In our quest to prepare new, second-generation ligands based on bpcd, we have instituted Knoevenagel condensation reactions between bpcd and selected aldehydes [9]. Here the union of the bpcd platform with a redox-active appendage and/or light-harvesting moiety facilitates, in theory, the tuning of the HOMO–LUMO gap and emission properties in a given metal complex. We have successfully employed this concept in the synthesis of several new ligands [10], with Eq. (1) showing the reaction for the preparation of 2-(ferrocenylidene)-4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (fbpcd) [11]. The dynamic isomerization of this particular ligand has been investigated in the triosmium clusters 1,2-Os_3(-CO)$_{10}$(fbpcd) and 1,2-$Os_3(CO)_{10}$(fbpcd) [11], and its redox properties have been recently reported in the case of the platinum(II) complex Pt(mnt)(fbpcd) [10b].



(1)

Given the importance of d^6 complexes in multicomponent redox relays [12], coupled with our interest in the coordination chemistry of the fbpcd ligand with different metal systems, we have prepared and examined the redox properties of the new rhenium(I) compound *fac*-BrRe$(CO)_3$(fbpcd) (**2**). The synthesis of the conjugated enyne derivative of fbpcd, whose structure is depicted below, and its use as a ligand in the synthesis of *fac*-BrRe$(CO)_3$(fpbpcd) (**3**) are also described herein.



fpbpcd

2. Experimental

2.1. Materials and equipment

The BrRe$(CO)_5$ employed in the synthesis of BrRe$(CO)_3(THF)_2$ (**1**) was prepared from $Re_2(CO)_{10}$ [13]. **1** was prepared according to the published procedure and typically used within one week of preparation [14]. The bpcd ligand used in the synthesis of the title diphosphines fbpcd and fpbpcd was synthesized from 4,5-dichloro-4-cyclopenten-1,3-dione and Ph_2PSiMe_3 [15], with the former ferrocene-containing ligand prepared from ferrocenecarboxaldehyde and bpcd [11]. The acetylferrocene used in the preparation of 3-ferrocenylpropynal [16] was synthesized according the procedure of Parshall et al. [17]. $Re_2(CO)_{10}$ was purchased from Pressure Chemical Co., while the chemicals ferrocene, ferrocenecarboxaldehyde, hexachlorocyclopentadiene, and diethyl chlorophosphate were purchased from Aldrich Chemical Co. and used as received. The reaction and NMR solvents employed in these studies were distilled from an appropriate drying agent under argon using Schlenk techniques or obtained from an Innovative Technology solvent purification system. All distilled solvents were stored in Schlenk storage vessels equipped with high-vacuum Teflon stopcocks [18]. The tetra-*n*-butylammonium perchlorate (TBAP) electrolyte was purchased from Johnson Matthey Electronics and recrystallized from hexane/ethyl acetate and dried under vacuum for at least 36 h prior to use.

The IR spectra were recorded on a Nicolet 6700 FT–IR spectrometer in amalgamated NaCl cells capable of handling air-sensitive samples. The quoted ^1H and ^{31}P NMR spectral data were recorded at 500 and 201 MHZ, respectively, on a Varian VXR-500 spectrometer. The ^{31}P NMR spectra were collected in the proton-decoupled mode and the reported chemical shifts referenced to external H_3PO_4 (85%), taken to have δ=0. UV–Vis spectra for **2** and **3** were recorded on a Hewlett–Packard 8452A diode array spectrometer in Schlenk-modified 1.0 cm quartz UV–Vis cells. The ESI-APCI mass spectra were recorded at the University of the Pacific (**2**) and UNT (**3**) mass spectrometry facilities, respectively, in the positive ionization mode. The matrices employed for the collection of the mass spectra were MeOH (**2**) and MeCN/KI (**3**).

2.2. Synthesis of fac-BrRe(CO)$_3$(fbpcd) (2) from BrRe(CO)$_3$(THF)$_2$ (1) and fbpcd

To a small Schlenk tube under argon flush was charged 0.10 g (0.20 mmol) of **1** and 0.14 g (0.21 mmol) of fbpcd, followed the addition of 25 mL of CH_2Cl_2 via syringe. The solution was stirred at room temperature for 1 h and then examined by IR analysis, which revealed the consumption of **1** and the presence of the desired product. The volatiles were removed under vacuum and the crude residue recrystallized from toluene at −20 °C. **2** was isolated by filtration under argon as an air-sensitive, purple-blue solid in 95% yield (0.19 g). IR (CH_2Cl_2): ν(CO) 2040 (vs), 1966 (s), 1912 (s), 1720 (w, sym dione), 1676 (s, antisym dione) cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} 358 (ε=6100), 578 (ε=1500). ^1H NMR ($CDCl_3$): δ 4.19 (s, 5H, Cp), 4.81 (s, 1H, Cp), 4.85 (s, 1H, Cp), 4.98 (s, 1H, Cp), 5.35 (s, 1H, Cp), 7.36–7.91 (m, 21H, alkenyl and aryl). ^{31}P NMR ($CDCl_3$): δ 23.03 (d, $^3J_{P-P}$=11 Hz), 23.55 (s, $^3J_{P-P}$=11 Hz). ESI–MS: *m/z* 1033.59 for $[\mathbf{2}+Na]^+$ and 1012.90 for $[\mathbf{2}+H]^+$.

2.3. Synthesis of fpbpcd from bpcd and 3-ferrocenylpropynal

0.10 g (0.22 mmol) of bpcd and 51 mg (0.22 mmol) of 3-ferrocenylpropynal in 30 mL of a 5:1 mixture of CH_2Cl_2/MeOH were stirred in the presence of 3 Å molecular sieves for 48 hr at room temperature. The solution slowly acquired a green–blue color indicative of the condensation product fpbpcd, and TLC analysis using CH_2Cl_2 as an eluent confirmed the presence of trace amounts of the starting materials and a prominent green–blue streak belonging to the desired ligand (R_f = 0.5). The solution was filtered under argon and the volatiles removed under vacuum, after which the residue was washed with hexane to remove the unreacted bpcd and 3-ferrocenylpropynal. Yield of green–blue fpbpcd: 0.10 g (68%). Given the air sensitivity of the product and the poor quality NMR spectra obtained due to paramagnetic impurities, the fpbpcd ligand was characterized by IR spectroscopy and used directly in the next step. IR (CH_2Cl_2): ν(CO) 1715 (w, sym dione), 1674 (s, antisym dione) cm^{-1}.

2.4. Synthesis of fac-BrRe(CO)$_3$(fpbpcd) (3) from BrRe(CO)$_3$(THF)$_2$ (1) and fpbpcd

The synthesis of **3** followed the procedure outlined for **2**. Here 0.10 g (0.20 mmol) of **1**, 0.14 g (0.20 mmol) of fpbpcd, and 25 mL of CH_2Cl_2 were stirred at room temperature for 1 h. IR analysis at this point confirmed the presence of the desired product, after which the solution was dried under vacuum to afford crude **3**. Recrystallization of **3** from toluene at −20 °C, followed by filtration under argon, gave **3** as an air-sensitive, green–blue solid in 91% (0.19 g). IR (CH_2Cl_2): ν(CO) 2041 (vs), 1967 (s), 1914 (s), 1729 (w, sym dione), 1687 (s, antisym dione) cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} 394 (ε = 12000), 608 (ε = 3800). ^1H NMR ($CDCl_3$): δ 4.27 (s, 5H, Cp), 4.54 (bs, 20H, Cp), 4.67 (bs, 2H, Cp), 6.80 (s, 1H, alkenyl), 7.15–7.81 (m, 2H, aryl). ^{31}P NMR ($CDCl_3$): δ 22.76 (d, $^3J_{P-P}$=12 Hz), 23.90 (s, $^3J_{P-P}$=12 Hz). ESI–MS: m/z 1073.13 for $[\mathbf{3}+K]^+$.

2.5. Electrochemical studies

The quoted cyclic voltammetric data were recorded on a PAR Model 273 potentiostat/galvanostat, equipped with positive feedback circuitry to compensate for *i*R drop. The cyclic voltammograms were recorded under oxygen- and moisture-free conditions in a homemade three-electrode cell. A platinum disk was utilized as the working and auxiliary electrode, and the reference electrode utilized a silver wire as a quasi-reference electrode, with the reported potential data standardized against the formal potential of the $Cp^*_2Fe/Cp^*_2Fe^+$ (internally added) redox couple, taken to have $E_{1/2}$=−0.20 V [19].

2.6. Extended Hückel MO calculations

The extended Hückel calculations on compounds **2** and **3** were carried out using the original program developed by Hoffmann [20], as modified by Mealli and Proserpio [21]. The weighted H_{ij}'s contained in the program were used in the calculations, and the input Z-matrices were constructed by using the available X-ray data for **3** and related compounds.

2.7. X-ray crystallographic data

Single crystals of $\mathbf{3} \cdot 1/2H_2O$ suitable for X-ray diffraction analysis were grown from an acetone solution containing **3** that had been layered with Et_2O. The X-ray data were collected on an APEX II CCD-based diffractometer at 100(2) K. The frames were integrated with the available APEX2 [22] software package using a narrow-frame algorithm, and the structure was solved and refined using the SHELXTL program package [23]. The molecular structure was checked using PLATON [24], and all nonhydrogen atoms were refined anisotropically. Except for the water solvent whose hydrogens were not located, all other hydrogen atoms were assigned calculated positions and allowed to ride on the attached carbon atom. The refinement for $\mathbf{3} \cdot 1/2H_2O$ converged at R = 0.0165 and $wR2$ = 0.0432 for 8316 independent reflection with $I > 2\sigma(I)$. The X-ray data and processing parameters are reported in Table 1, with selected bond distances and angles quoted in Table 2.

Table 1
X-ray crystallographic data and processing parameters for $\mathbf{3} \cdot 1/2H_2O$.

CCDC entry number	727855
Cryst system	triclinic
Space group	$P\bar{1}$
a (Å)	10.0766(3)
b (Å)	10.5463(4)
c (Å)	19.0710(7)
α (°)	92.612(1)
β (°)	101.511(1)
γ (°)	98.580(1)
V ($Å^3$)	1957.8(1)
Mol formula	$C_{44}H_{30}BrFeO_5P_2Re \cdot 1/2H_2O$
Formula weight	1043.60
Formula units per cell (Z)	2
D_{calcd} (Mg/m^3)	1.770
λ (Mo Kα) (Å)	0.71073
μ (mm^{-1})	4.610
Absorption correction	semi-empirical from equivalents
Absorption correction factor	0.8371/0.4042
Total reflections	23813
Independent reflections	8316
Data/res/parameters	8316/0/505
R_1[a] [$I \geqslant 2\sum(I)$]	0.0165
wR_2[b] (all data)	0.0432
GOF on F^2	1.103
$\Delta\rho$ (max), $\Delta\rho$ (min) ($e/Å^3$)	1.142, −0.503

[a] $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$.
[b] $R_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond distances (Å) and angles (deg) in $\mathbf{3} \cdot 1/2H_2O$.

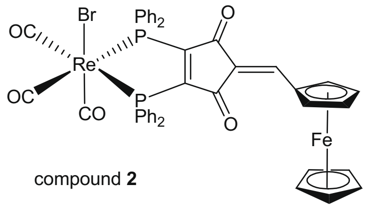
Bond distances			
Re(1)–C(1)	1.952(2)	Re(1)–C(2)	1.970(2)
Re(1)–C(3)	1.918(2)	Re(1)–Br(1)	2.6333(2)
Re(1)–P(1)	2.4373(6)	Re(1)–P(2)	2.4601(6)
C(4)–C(8)	1.349(3)	C(4)–C(5)	1.507(3)
C(7)–C(8)	1.513(3)	C(6)–C(7)	1.475(3)
C(5)–C(6)	1.478(3)	C(6)–C(33)	1.349(3)
C(33)–C(34)	1.405(3)	C(34)–C(35)	1.204(3)
C(35)–C(36)	1.419(3)	P(1) ··· P(2)	3.1810(8)
Fe(3)-centroid[a]	1.654(3)	Fe(3)-centroid[b]	1.660(3)
Bond angles			
C(2)–Re(1)–P(1)	173.17(7)	C(1)–Re(1)–P(2)	166.09(7)
P(1)–Re(1)–P(2)	81.01(2)	P(1)–Re(1)–Br(1)	88.89(1)
P(2)–Re(1)–Br(1)	80.29(2)	O(1)–C(1)–Re(1)	176.8(2)
O(2)–C(2)–Re(1)	179.6(3)	O(3)–C(3)–Re(1)	177.8(2)
C(33)–C(6)–C(7)	128.0(2)	C(33)–C(6)–C(5)	124.3(2)
C(6)–C(33)–C(34)	126.1(2)	C(35)–C(34)–C(33)	173.6(3)
C(34)–C(35)–C(36)	177.6(3)		

[a] Mean Fe(3)–C distance for the Cp carbons C(36)–C(40).
[b] Mean Fe(3)–C distance for the Cp carbons C(41)–C(45).

3. Results and discussion

3.1. Synthesis, spectroscopic data, and redox properties of *fac*-$BrRe(CO)_3$(fbpcd) (**2**)

Displacement of the THF ligands in $BrRe(CO)_3(THF)_2$ (**1**) by fbpcd is rapid and gives **2** in essentially quantitative yield as assessed by IR spectroscopy. While **2** may be isolated by column chromatography over silica gel, this leads to considerable material loss and oxidation of the ferrocene appendage, which in turn introduces unwanted paramagnetic impurities in the NMR sample. Alternatively, **2** could be isolated by recrystallization in toluene at low temperature in high yield, making this the preferred method of isolation. We would add that **2** may also be prepared by heating $BrRe(CO)_5$ in the presence of fbpcd but the yield of **2** is lower and the reaction is accompanied by decomposition, complicating the purification of the desired product. **2** is mildly air sensitive, especially in solution, but may be handled in the atmosphere for a short period of time. The structure of **2** is shown below.



compound **2**

2 was thoroughly characterized by IR, NMR, and UV–Vis spectroscopies, and mass spectrometry. The IR spectrum revealed terminal carbonyl stretching bands at 2041 (vs), 1967 (s), and 1914 (s) cm^{-1} characteristic of the signature *fac*-$Re(CO)_3$ moiety [25], in addition to two lower energy ν(CO) bands observed at 1729 (w) and 1687 (s) cm^{-1} ascribed to the vibrationally coupled symmetric and antisymmetric carbonyl stretching bands associated with the dione platform [26]. The ^1H NMR spectrum exhibited a 5H singlet at δ 4.19 for the unsubstituted Cp ring, with the alkenyl-substituted Cp ring displaying four 1H singlets at δ 4.81, 4.85, 4.98, and 5.35. The lone alkenyl hydrogen and the aromatic hydrogens appear as a set of overlapping resonances from δ 7.36–7.91. Two inequivalent ^{31}P resonances were observed in the ^{31}P NMR spectrum of **2** at δ 23.03 and 23.55 consistent with the formulated structure. The ESI mass spectrum of **2** revealed a strong molecular ion for the sodium-containing species $[\mathbf{2}+Na]^+$ based on a *m/z* peak at 1033.59, along with a weak *m/z* peak at 1012.90 for $[\mathbf{2}+H]^+$. Finally, the UV–Vis spectrum of **2** (Fig. 1) recorded in CH_2Cl_2 showed two featureless bands at 358 and 578 nm, whose assignments are ascribed to a $d\pi(Re) \rightarrow \pi^*(dione)$ MLCT and a charge-transfer-to-solvent (CTTS) transition involving the ferrocene and CH_2Cl_2, respectively [5a,27].

The redox properties of **2** were examined by cyclic voltammetry (CV) in CH_2Cl_2 containing 0.25 M TBAP as the supporting electrolyte. The CV of **2** (not shown) recorded over the potential range of 1.0 V to −1.0 V and at a scan rate of 250 mV/s revealed two diffusion-controlled waves at $E_{1/2} = 0.71$ and −0.65 V belonging to $0/1^+$ and $0/1^-$ redox couples [28]. The site of the two redox waves was verified by extended Hückel MO calculations, which revealed HOMO and LUMO levels at −11.80 eV and −10.42 eV, respectively. The HOMO in **2** is best viewed as an iron-based d_{z2} orbital that is similar in nature to the a_{1g} HOMO found in ferrocene [29]. The computationally observed LUMO traces its parentage to the ψ_4 MO associated with the π system of dione ring, whose calculated energy and nodal pattern are in excellent agreement with those data reported for other bpcd-substituted compounds prepared by our groups [6a,10,30]. The relatively low energy of this π^* orbital renders it a superb electron reservoir and accounts nicely for the observed one-electron reduction found by CV.

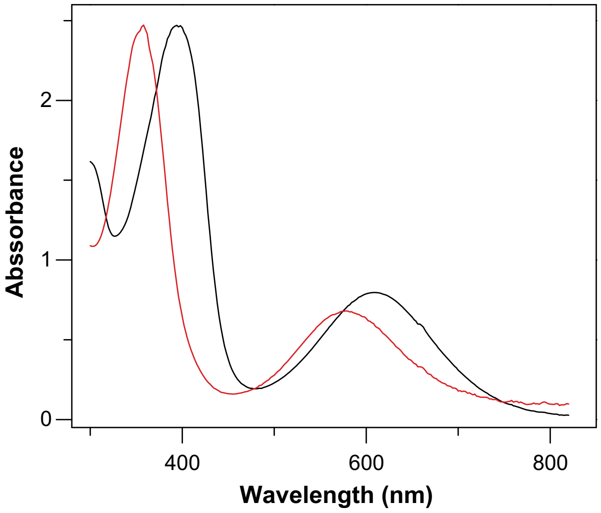


Fig. 1. UV–Vis spectra for **2** (red line; ca. 4e-4 M) and **3** (black line; ca. 2e-4 M) in CH_2Cl_2 solvent. The ordinate values displayed are for **2**, with **3** plotted alongside using arbitrary absorbance units.

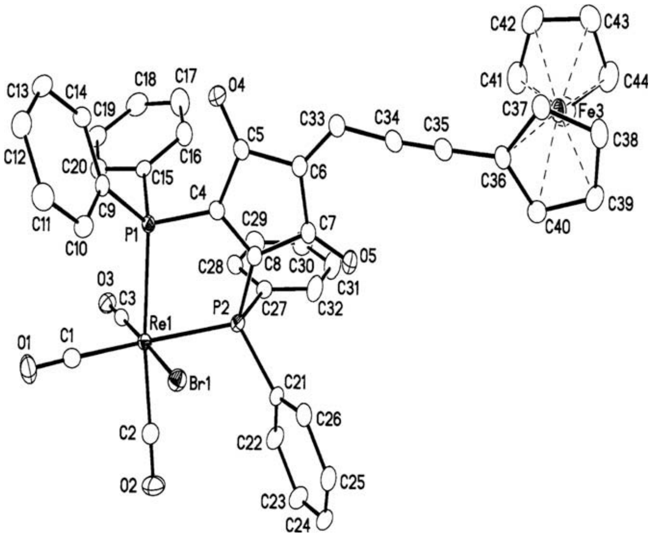
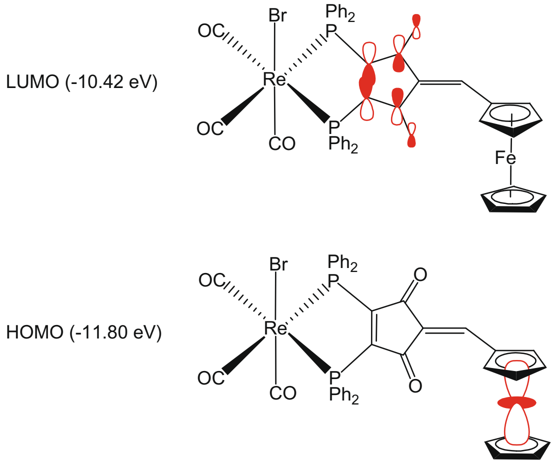


Fig. 2. Perspective view of $\mathbf{3} \cdot 1/2H_2O$ showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecule has been omitted for clarity.



3.2. Synthesis, spectroscopic data, and redox properties of fac-$BrRe(CO)_3$(fpbpcd) (3)

Knoevenagel condensation of 3-ferrocenylpropynal with an equimolar amount of bpcd in a solvent mixture composed of CH_2Cl_2/MeOH (5:1) in the presence of 3 Å molecular sieves, whose function is to absorb the liberated water, furnishes the new ligand 2-(3-ferrocenylprop-2-ynylidene)-4,5-bis(diphenylphosphino)4-cyclopenten- 1,3-dione (fpbpcd). Isolated yields of fpbpcd were on the order of ca. 70% for samples that were purified by recrystallization. The fpbpcd ligand exhibits a green–blue color and undergoes facile oxidation in solution upon exposure to oxygen, making characterization of the ligand by NMR spectroscopy problematic. The IR spectrum of the ligand revealed two ν(CO) bands at 1715 (w) and 1674 (s) for the kinematically coupled dione carbonyl groups consistent with the proposed structure.

Treatment of either $BrRe(CO)_5$ or **1** with a slight excess of fpbpcd affords the corresponding diphosphine-substituted compound **3**, whose structure is depicted below. As discussed earlier, reactions using **1** as a starting material were cleaner and afforded **3** in higher yields. **3** was isolated by recrystallization as a

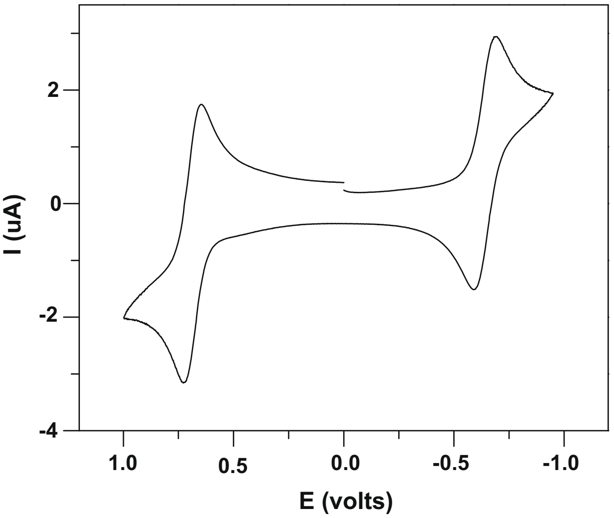
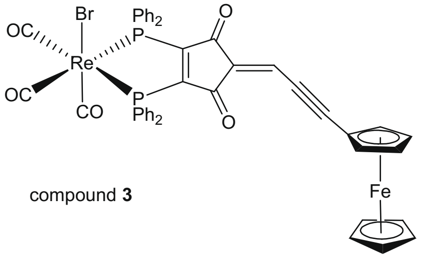


Fig. 3. Cathodic scan cyclic voltammogram of **3** (ca. 10^{-3} M and 0.25 V/s) in CH_2Cl_2 containing 0.25 M TBAP at room temperature.

green–blue solid and was characterized by a combination of IR, NMR, and UV–Vis spectroscopies, mass spectrometry, and X-ray diffraction analysis. The IR spectrum for **3** reveals terminal ν(CO) bands at 2041 (vs), 1967 (s), and 1914 (s) cm^{-1}, along with symmetric and antisymmetric dione ν(CO) bands at 1729 and 1687 cm^{-1}. These carbonyl frequencies relative to those recorded for **2** indicate that the electron-donating properties of the two diphosphine ligands are similar in magnitude. The UV–Vis spectrum (Fig. 1) shows a slight bathochromic shift of the two principal absorption bands compared to **2**, with maxima appearing at 394 nm and 608 nm. The spectroscopic assignments for these UV–Vis bands are assumed to be the same as those in **2** (*vide supra*). The ^{1}H NMR spectrum shows the cyclopentadienyl hydrogens at δ 4.27, 4.54, and 4.67 in a 5:2:2 integral ratio, and the lone vinyl hydrogen on the enyne chain appears as a singlet at δ 6.80. The aromatic hydrogens were observed as a multiplet from δ 7.15–7.81. The inequivalent phosphines in **3** appear as doublets in the ^{31}P NMR spectrum at δ 22.76 and 23.90 and exhibit a $^3J_{P-P}$ coupling of 12 Hz. The ESI mass spectrum recorded in MeCN/KI gave a strong molecular ion at *m/z* 1073.13 for $[\mathbf{3}+K]^+$ consistent with the formulated structure.



compound **3**

The unequivocal identity of **3** and the presence of the enyne linking moiety that serves to tether the bpcd and ferrocene groups were established by X-ray diffraction analysis. The solid-state structure of $\mathbf{3} \cdot 1/2H_2O$ is depicted in Fig. 2. The rhenium center is six-coordinate with the fpbpcd ligand situated *trans* to two of the three facial CO groups. The mean Re–P bond distance of 2.4487 Å and the bond angle of 81.01(2)° for the P(1)–Re(1)–P(2) linkage agree with those values reported for the octahedral rhenium(I) compounds *fac*-$BrRe(CO)_3$(bma) [5a], *fac*-$BrRe(CO)_3$(tbpcd) [10c], $ReCl_2[(Z)\text{-}Ph_2PCH{=}CHPPh_2]_2$ [31], and $ClRe(CO)_3[3,4\text{-}Me_2\text{-}3',4'\text{-}$ bis(diphenylphosphino)tetrathiafulvalene] [32]. The Re–CO bond distances range from 1.970(2) Å [Re(1)–C(2)] to 1.918(2) Å [Re(1)–C(3)] with the latter axial CO group displaying the shortest Re–CO bond distance. The Re(1)–Br(1) vector reveals a bond length of 2.6333(2) Å, whose value is in excellent agreement with the Re–Br distance found in the diphosphine-substituted compounds *fac*-$BrRe(CO)_3[\eta^2\text{-}(Ph_2PCH_2)_3CMe]$ [33], *fac*-$BrRe(CO)_3[Ph_2PO(CH_2)_2OPPh_2]$ [34], and *fac*-$BrRe(CO)_3[1,2\text{-}(HOCH_2P)_2C_6H_4]$ [35]. The five-membered metallocyclic ring defined by the atoms Re(1)–P(2)–C(8)–C(4)–P(1) is distinctly non-planar and exhibits a fold angle of 29.49(4)° along the P(1) $\cdots$ P(2) hinge. The enyne carbons are nearly planar on basis of the observed torsion angle of ca. −165° for the C(6)–C(33)–C(34)–C(35) atoms. The remaining bond distances and angles are unremarkable and require no comment.

The cyclic voltammetric properties of **3** were examined in CH_2Cl_2 under conditions identical to those employed in the investigation of **2**. The CV of **3**, which is shown in Fig. 3, recorded over the potential range of 1.0 V to −1.0 V and at a scan rate of 250 mV/s revealed well-defined diffusion-controlled waves at $E_{1/2} = 0.68$ and −0.65 V ascribed to $0/1^+$ and $0/1^-$ redox couples. These half-wave potentials are identical to those redox data recorded for **2**, suggesting identical HOMO and LUMO levels in the two different rhenium(I) products. This latter assumption was subsequently corroborated by extended Hückel MO calculations, which revealed HOMO and LUMO levels at −11.86 eV and −10.39 eV, respectively. The orbital composition of these important frontier molecular orbitals in **3** resembles the HOMO and LUMO levels computed for **2** and will not be reproduced here.

4. Conclusions

The new rhenium(I) compounds *fac*-$BrRe(CO)_3$(fbpcd) (**2**) and *fac*-$BrRe(CO)_3$(fpbpcd) (**3**) have been synthesized and their redox properties investigated by cyclic voltammetry. Both compounds exhibit well-defined $0/1^+$ and $0/1^-$ redox couples attributed to ferrocene oxidation and diphosphine reduction, respectively, with the HOMO and LUMO compositions in **2** and **3** corroborated by extended Hückel MO calculations. The π^*-based LUMO in compounds **2** and **3** is localized on the dione platform and remains unchanged to that found in the parent bpcd ligand. The selection of aldehydes more electron rich than ferrocenecarboxaldehyde will facilitate the tuning of the HOMO level in our bpcd-derived condensation products, and this aspect is under active investigation. Future time-resolved photophysical studies are planned and these data will be disseminated in due course.

5. Supplementary data

CCDC 727855 contains the supplementary crystallographic data for $\mathbf{3} \cdot 1/2H_2O$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; Fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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