Synthesis and optoelectronic properties of transition metal complexes incorporating dithieno[3,2-*b*:2',3'-*d*]phosphole ligands

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A series of dithieno[3,2-*b*:2',3'-*d*]phosphole-based transition metal complexes, including Au, Fe, Pt, Rh and W as central metals have been synthesised and characterised. Structural investigations by X-ray single crystal crystallography supported the high degree of π -conjugation in the dithienophosphole ligands. This essential requirement for potential applications in molecular electronics and optoelectronics provides small band gaps for the materials. Investigations toward the optoelectronic properties of the respective complexes by fluorescence spectroscopy indicated that systematic alterations of the electronic structure are connected to different variables such as transition metal employed, functionalisation of the dithienophosphole ligands as well as complex geometries. The investigated Pt-based complexes exhibit only poor photoluminescence whereas Rh-, W- and Fe-based species with silyl functionalised dithienophosphole ligands show appreciable photophysical properties. The Au complexes investigated exhibit strong photoluminescence properties with very intriguing features in terms of excitation and emission wavelengths, intensity as well as selectivity.

Introduction

The incorporation of phosphorus centres into functional π conjugated as well as polymeric materials is an area of growing interest.1 The versatile reactivity and electronic nature of trivalent phosphorus offers interesting opportunities for the development of new materials with unusual properties.² Its ability to react with oxidizing agents, its Lewis basicity which allows reactions with Lewis acids in addition to the potential for coordination to transition metals, offers a broad variety for tuning the electronic properties of phosphorus based materials by synthetically facile modifications that are not possible in this simplicity with genuine organic systems.³ In the context of an implementation into π conjugated systems, phosphole-moieties are of particular interest since they exhibit a reduced orbital interaction of the phosphorus lone-pair with the conjugated π -system resulting in a low degree of lone-pair delocalization.4-7 However, a weak interaction that is observed between the π^* -LUMO and the exocyclic σ^*_{PC} orbital, leads to an extraordinary electronic structure of the system with a low lying LUMO level that can be utilised in molecular electronics.^{1f,6d} We have recently established the reactivity and optoelectronic properties of the novel dithieno[3,2-b:2',3'-d]phosphole system and corresponding polymeric materials displaying very advantageous photophysical properties with respect to wavelength, intensity and tunability.8 In the context of our work we were able to show that simple chemical modifications carried out at the central phosphorus atom such as oxidation or complexation with Lewis acids afford dithienophosphole species with significantly altered optoelectronic properties. In this paper we now describe the synthesis and optoelectronic properties of a variety of transition metal complexes that display dithieno [3,2-b:2',3'-d] phosphole ligands to

explore the suitability of a metal functionalisation for the fine tuning of the optoelectronic properties of the dithienophosphole system which could then potentially be applied in functional materials.

Results and discussion

Synthesis of the complexes

With the utility in optoelectronic molecular or polymeric materials in mind, we targeted transition metal complexes of dithienophospholes that are conveniently accessible *via* simple chemical modifications and afford the metal functionalised systems in high, desirably quantitative, yields. We therefore focused on transition metals that are known to form strong bonds with phosphane ligands and complexes that are fairly persistent under aerobic conditions.

To compare the influence of different complex configurations on the optoelectronic properties of our materials we first synthesised a series square planar Pt based dithienophosphole complexes that were expected to exhibit *cis*-configuration as observed for bis(dibenzophosphole)platinum(II) halides.9 A related Pd based dithienophosphole complex ([A]₂PdCl₂^{8a}) shows trans-configuration in the solid state allowing for a convenient investigation of the differences between configuration isomers. The platinum complexes 1A, 1B and 1C are accessible by reaction of K_2 PtCl₄ with two equivalents of the corresponding dithienophosphole A, B or C in dichloromethane at room temperature in almost quantitative yields (Scheme 1). Compared to the free ligands (A: $\delta^{31}P = -25.0$;^{8a} **B**: $\delta^{31}P = -27.4$;^{8a} **C**: $\delta^{31}P = -21.5^{8b}$), their ³¹P NMR spectra show single resonances that are slightly shifted downfield upon complexation (1A: $\delta = -9.2$; 1B: $\delta = -10.5$; 1C: $\delta = -7.6$) and exhibit the typical satellites due to the presence of Pt (1A: $J(P, {}^{195}Pt) = 3508$ Hz; 1B: $J(P, {}^{195}Pt) = 3511$ Hz; 1C: $J(P,^{195}Pt) = 3506$ Hz). According to the P,¹⁹⁵Pt-coupling constants

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only cis-configured isomers are generated.¹⁰ This is in contrast to the observations made with the related Pd-complex where both configuration isomers (ratio *trans* : cis = 3 : 1) were observed in solution,^{8a} which can be attributed to the lower kinetic stability of Pd-phosphane complexes. The ¹H and ¹³C NMR data relate to those of the Pd-complex [A]₂PdCl₂^{8a} with a pseudo triplet splitting for most of the ¹³C NMR resonances due to the coupling to the two different phosphorus centres located at the same and the adjacent dithienophosphole ligand. Although we were able to obtain suitable single crystals for X-ray structure studies of the Pt complexes from different solvents (toluene, xylenes, acetonitrile), no satisfying structure determination could be achieved due to some significant disorder as well as the presence of a variable amount of strongly disordered solvent molecules within the unit cell. The cis-configuration of the complexes, however, which is most likely the reason for the unfavourable packing in the solid state, was undoubtedly confirmed by these investigations.

Since (phosphanyl)gold(I) complexes often have been found to exhibit interesting luminescence properties¹¹ that can be used in e.g. organic light-emitting diodes (OLEDs), as shown by Réau and co-workers, 6c,d we also synthesised dithienophospholebased Au(I) chloride complexes. Starting from the two differently functionalised dithienophospholes A and B.^{8a} complexes 2A and 2B were obtained in a quantitative reaction with (tht)AuCl in CH₂Cl₂ in very good isolated yields. The ³¹P NMR spectra of both complexes again show low field shifted NMR resonances at $\delta^{31}P =$ 1.9 for **2A** and $\delta^{31}P = 2.1$ for **2B** confirming the complexation of the phosphorus centre. The ¹H and ¹³C NMR data relate to those observed for the free ligands^{8a} with the exception that the ¹H NMR signals of the phenyl substituent are shifted downfield which is indicative of the metal functionalisation. These data support the, compared with the free ligands, significantly increased acceptor character of the central phosphorus atom affording a decrease of the energy of the dithienophosphole π^* -LUMO^{8a} and thus optimising the electronic structure of the system. We were able to obtain suitable single crystals for an X-ray structure determination of 2B from a concentrated pentane solution kept at 4 °C. The molecular structure of 2B in the solid state is related to that of the corresponding dithienophosphole oxide $[B]=O^{8a}$ with the

expected planar geometry of the rigid tricyclic dithienophosphole, displaying an anti-configuration of the two thiophene moieties and the phosphole unit. The high degree of π -conjugation, apparent in the short C-C-single bonds and the elongated C-C-double bonds of the fused ring systems of the ligand (see Fig. 1), as well as the transoid anti-arrangement of the tBuSiMe₂ groups are similar to the related dithienophosphole oxide $[B]=O.^{8a}$ The Au centre shows an almost linear coordination (P1-Au1-Cl1 177.26(4)°) with bond lengths of 2.2249(12) Å for Au1–P1 and 2.2946(12) Å for Au1-Cl1 that are typical for (phosphanyl)gold(I) chlorides.¹² No aurophilic interactions are observed in the solid state (closest Au-Au distance *ca*. 5.639 Å)¹³ but intermolecular interactions can be noticed between the gold centre and some hydrogen atoms located at a thiophene unit (distance ca. 3.156 Å) as well as the phenyl substituents (distances ca. 2.949 and 2.911 Å) of neighbouring molecules.



Fig. 1 Molecular structure of **2B** in the solid state (50% probability level). Selected bond lengths (Å) and angles (°): Au1–P1 2.2249(12), Au1–C11 2.2946(12), P1–C3 1.814(4), P1–C6 1.803(4), P1–C11 1.814(4), C1–C2 1.370(6), C2–C3 1.412(6), C3–C4 1.378(6), C4–C5 1.460(6), C5–C6 1.382(6), C6–C7 1.433(6), C7–C8 1.373(6); P1–Au1–C11 177.26(4), C6–P1–C3 91.6(2).

With a potential utility as catalyst system for future investigations in mind, we synthesised the corresponding rhodium complexes based on the dithienophosphole system. The Rh(cod)Clfunctionalised dithienophospholes are accessible in a quantitative reaction of the corresponding dithienophospholes **A** and **B**^{8a} with half an equivalent of [Rh(cod)Cl]₂ in thf at room temperature to afford the desired rhodium complexes in good isolated yields. The ³¹P NMR chemical resonances of **3A** and **3B** show a stronger lowfield shift compared to the Pt- and Au-complexes with $\delta^{31}P =$ 11.5 for **3A** and $\delta^{31}P = 10.5$ for **3B** and exhibit the significant doublet splitting (*J*(P,Rh) = 148.3 Hz for both compounds).¹⁴ The ¹H and ¹³C NMR data relate to those of the Au-complexes **2A** and **2B**. The presence of four distinct resonances for the coordinated cyclooctadiene ligand, furthermore supports a square planar complex geometry in solution, as expected.¹⁴

To further explore the effects of different complex geometries and varying numbers of dithienophosphole ligands on the optoelectronic properties, we synthesised a series of tungsten and iron carbonyl complexes exhibiting one or two dithienophosphole ligands, respectively. $W(CO)_6$ and $Fe(CO)_5$ were chosen since they provide different complex geometries (octahedral vs. trigonal bipyramidal) that were expected to afford different configurations for the corresponding disubstituted bis(dithienophosphole) complexes. The tungsten-based mono(dithienophosphole) complexes 4A and 4C were accessible in an almost quantitative reaction of the respective dithienophospholes A^{8a} and C^{8b} with $W(CO)_5$ thf at room temperature in thf and could be isolated in decent yields. The ³¹P NMR spectra of **4A** and **4C** show lowfield shifted resonances at $\delta^{31}P = -7.9$ for **4A** and $\delta^{31}P = -3.9$ for **4C**, that are similar to the Pt-based complexes supporting the increased acceptor character of the phosphorus centre. The ${}^{1}J(\mathbf{P},{}^{183}\mathbf{W})$ coupling constants of 227.9 Hz for 4A and 230.0 Hz for 4C also confirm the complexation of the phosphorus centre by a tungsten atom.¹⁵ The ¹H and ¹³C NMR data again relate to the other complexes presented in this paper. The same is true for the mono(dithienophosphole)iron carbonyl complex 5A that is accessible by reaction of A with

Table 1 Crystallographic data for 2B, 4A and 6C

Fe₂(CO)₉ in thf at room temperature. The ³¹P NMR resonance of **5A** shows the most significant low field shift of all the herein presented complexes at $\delta^{31}P = 49.9$.

Suitable single crystals for an X-ray structure determination (Table 1) of the tungsten complex **4A** were obtained from a concentrated toluene solution kept at -30 °C. The molecular structure of **4A** in the solid state shows an octahedral complex geometry with the W(CO)₅-fragment capping the phosphorus centre, as expected (Fig. 2). The bond lengths of the coordinated dithienophosphole ligand correspond to those of the related gold complex **2B** (Table 1) and other structurally known



Fig. 2 Molecular structure of **4A** in the solid state (50% probability level). One toluene solvent molecule is omitted for clarity. Selected bond lengths (Å) and angles (°): W1–P1 2.5028(5), W1–C45 2.009(2), W1–C41 2.043(2), W1–C42 2.037(2), W1–C43 2.053(2), W1–C44 2.053(2), P1–C3 1.824(2), P1–C6 1.819(2), P1–C31 1.826(2), C1–C2 1.375(3), C2–C3 1.420(3), C3–C4 1.377(3), C4–C5 1.452(3), C5–C6 1.383(3), C6–C7 1.414(3), C7–C8 1.373(3); P1–W1–C45 175.80(6), C6–P1–C3 90.14(10).

Compound	2B	4A	6C
Formula M_r T/K Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $V/Å^3$ $Z, D_c/Mg \text{ cm}^{-3}$ F(000) $\mu(Mo-Ka)/mm^{-1}$ θ Range for data collection/ $^{\circ}$ Reflections collected/unique (R_{int}) Data/restraints/parameters Final R indices [$I > 2\sigma(I)$] R indices (all data) $GOE \text{ cn } E^2$	$\begin{array}{c} C_{26}H_{37}AuCIPS_{2}Si_{2}\\ 733.24\\ 110(2)\\ Monoclinic\\ P2_{1}/c \ (no.\ 14)\\ 16.279(3)\\ 13.492(3)\\ 14.313(3)\\ 90\\ 91.33(3)\\ 90\\ 91.33(3)\\ 90\\ 3142.7(11)\\ 4,\ 1.550\\ 1456\\ 5.040\\ 1.25-28.02\\ 25336/7583 \ (0.0427)\\ 7583/0/298\\ R1 = 0.0338, \ wR2 = 0.0750\\ R1 = 0.0415, \ wR2 = 0.0876\\ 1.167\\ \end{array}$	$C_{25}H_{25}O_5PSSi_2W \cdot C_7H_8$ 786.65 110(2) Triclinic $P\overline{1}$ (no. 2) 11.1535(4) 11.5231(4) 14.0934(6) 85.359(1) 67.820(1) 72.751(1) 1600.87(11) 2, 1.632 778 3.898 2.06-30.05 28162/9031 (0.0292) 9031/15/378 $R1 = 0.0220, wR2 = 0.0519$ $R1 = 0.0220, wR2 = 0.0519$ $R1 = 0.0220, wR2 = 0.0525$ 1.069	$C_{32}H_{18}O_4P_2S_4W$ 840.49 110(2) Triclinic $P\overline{1}$ (no. 2) 11.179(2) 14.844(3) 18.518(4) 94.93(3) 95.76(3) 94.64(3) 3033.7(10) 4, 1.840 1640 4.227 1.11 to 28.47 47437/15170 (0.0481) 15170/0/775 R1 = 0.0310, wR2 = 0.0781 R1 = 0.0368, wR2 = 0.0811 1.048
Largest diff. peak and hole/e ${\rm \AA^{-3}}$	1.473 and -1.376	1.461 and -0.789	3.047 and −1.908

dithienophospholes⁸ with a significant degree of π -conjugation (long C–C-double and shortened C–C-single bonds). The P–C bonds lengths of 1.819(2) Å (P1–C6), 1.824(2) Å (P1–C3) and 1.826(2) Å (P1–C31) are slightly longer than the ones observed for **2B** indicating a reduced electron affinity of the W(CO)₅ group compared to the AuCl fragment in **2B**. The W1–P1 bond of 2.5028(5) Å can be related to other structurally known tungsten– phosphole complexes^{17,6a} and the W1–C45 bond of 2.009(2) Å (*trans*-CO) supports, compared with a carbonyl ligand-, a reduced π -acceptor character of the dithienophosphole (see *e.g.* W1–C41 2.043(2) Å (*cis*-CO)).

Introduction of a second dithienophosphole ligand can be achieved upon irradiation with UV-light of either the monosubstituted tungsten pentacarbonyl complex 4C in the presence of another equivalent of C or a mixture of two equivalents of A with one equivalent of Fe₂(CO)₉ to afford the bis(dithienophosphole) complexes 6C and 7A in good yields (Scheme 2). Compared with their mono-substituted congeners, the ³¹P NMR spectra show slightly lowfield shifted resonances at $\delta^{31}P = -2.9$; $J(P, {}^{183}W) =$ 225.0 Hz for **6C** (*cf.* δ^{31} P = -3.9; J(P,¹⁸³W) = 230.0 Hz for **4C**) and at $\delta^{31}P = 59.4$ for 7A (cf. $\delta^{31}P = 49.9$ for 5A). The presence of two resonance signals for the carbonyl carbon atoms in the ¹³C NMR spectrum of 6C at δ^{13} C = 202.9 and 200.7 supports a *cis*configuration of the two dithienophosphole ligands whereas the existence of only one carbonyl resonance at $\delta^{13}C = 212.7$ for 7A indicates a trans-configuration for the iron complex. The pseudo triplet splitting of most of the ¹³C NMR signals of 6C and 7A is similar to those observed for the Pd-8a and Pt-complexes 1A-C and corroborates the generation of bis(dithienophosphole) complexes.



We were able to obtain yellow single crystals of **6C** from a concentrated pentane–toluene (1 : 1) solution at -30 °C that were suitable for an X-ray structure determination. The molecular structure of **6C** (Table 1) in the solid state shows two independent, *cis*-configured, octahedral complex molecules in the unit cell whose geometry is governed by different intramolecular π -stacking interactions between the two dithienophosphole ligands. Whereas in one of the independent complex molecules the π -stacking is observed between the anellated dithienophosphole ring system and the phenyl group of the adjacent ligand, leading to a

kind of endo/exo complex conformation, the second molecule in the unit cell exhibits an almost coplanar arrangement of the two dithienophosphole planes with an exo/exo conformation (see Fig. 3). The C-C-bond lengths of the coordinated ligands support their high degree of π -conjugation.⁸ The *endocyclic* P–C bonds of the ligands (1.814(3)-1.827(3) Å) are only slightly shorter than the respective exocyclic P-C(phenyl) bonds (1.826(3)-1.830(3) Å) a feature that is also observed with the free ligand C.^{8b} Due to the complexation to W, these bonds experience some shortening and relate to those observed for 4A. The same is true for the W-P bonds of the endo/exo-complex conformer (W1-P1 2.4995(10) Å, W1–P2 2.5006(11) Å) whereas is the *exo/exo*-conformer their shortening is significantly more pronounced (W2-P3 2.4707(10) Å, W2–P4 2.4760(11) Å) which is most likely a result of the π stacking mode of the two dithienophosphole ligands. As observed for 4A, the bond lengths of trans-carbonyl groups (W-C ca. 1.99(1) Å) are also significantly shorter than the W-cis-CO bonds lengths of about 2.04(1) Å again supporting the reduced π -acceptor character of the dithienophosphole ligand.

Optoelectronic properties of the complexes

The photoluminescence of the dithienophosphole system opens up a great potential for applications in materials science and optoelectronics since the detection of fluorescence is a convenient analytical tool due to its highly sensitive, selective and safe nature. It allows, for example, the observation electronic transitions in progress;^{16,17} a change of the electronic structure of the materials should have an effect on their luminescence properties and thus reflecting its delocalisation and polarisation.¹⁸ Therefore, the functionalisation of optoelectronic materials by transition metals or their complexes, respectively, is an intriguing approach which can be conveniently achieved by means of trivalent phosphorus species, as already indicated.

Our investigations towards the influence of different transition metal moieties on the optoelectronic properties of the dithienophosphole system indicate that the systematic alteration of the electronic structure by this method is connected to a number of variables and not always predictable. It should be mentioned in this context that the fluorescence spectra (excitation and emission) of the presented dithienophosphole transition metal complexes are governed by *intra*-ligand π - π *-transitions. This is in coherence with the spectra of the free ligands A-C and their non-transition metal functionalised congeners.8 The transition metal complex species presented herein should therefore rather be described as transition metal-doped dithienophospholes. However, the electronic structure of the dithienophospholes used, the transition metals employed as well as the complex geometries play an important role for the resulting optoelectronic absorption and emission properties of the materials in terms of intensity. The corresponding maximum wavelengths, particularly for emission, on the other hand, do not seem to be affected by different transition metal moieties and complex geometries as much. Most of the complexes based on the ligands A and B presented in this paper show a maximum wavelength of their emission at 460/461 nm, whereas the systems based on the ligand C show a wider range of emission wavelengths between 437 and 451 nm (see Table 2). This red-shift of about 10-20 nm of the silvl functionalised dithienophosphole complexes is similar to the free ligands A





Fig. 3 Molecular structure of **6C** in the solid state (50% probability level). Selected bond lengths (Å) and angles (°): *endo/exo*-conformer: W1–P1 2.4995(10), W1–P2 2.5006(11), W1–C3 1.986(4), W1–C4 1.999(3), W1–C1 2.042(3), W1–C2 2.045(3), P1–C13 1.825(3), P1–C17 1.814(3), P1–C101 1.833(3), P2–C23 1.819(3), P2–C26 1.811(3), P2–C201 1.826(3), C11–C12 1.356(5), C12–C13 1.417(4), C13–C14 1.374(4), C14–C15 1.457(4), C15–C17 1.375(4), C17–C16 1.420(4), C16–C18 1.353(4), C21–C22 1.356(5), C22–C23 1.422(5), C23–C24 1.372(5), C24–C25 1.449(5), C25–C26 1.372(5), C26–C27 1.425(5), C27–C28 1.374(5); P1–W1–C4 177.85(9), P2–W1–C3 172.46(10); *exo/exo*-conformer: W2–P3 2.4760(101), W2–P4 2.4707(10), W2–C7 1.994(4), W2–C8 2.014(4), W2–C5 2.044(3), W2–C6 2.040(3), P3–C33 1.819(3), P3–C36 1.820(3), P3–C301 1.830(3), P4–C43 1.822(3), P4–C46 1.827(3), P4–C401 1.830(3), C31–C32 1.364(5), C32–C33 1.418(4), C33–C34 1.382(4), C34–C35 1.448(4), C35–C36 1.378(4), C36–C37 1.411(4), C37–C38 1.365(5), C41–C42 1.353(5), C42–C43 1.427(4), C43–C44 1.374(4), C44–C45 1.441(4), C45–C46 1.374(4), C46–C47 1.415(4), C47–C48 1.365(4); P3–W2–C7 179.97(12), P4–W2–C8 179.11(10).

 Table 2
 Fluorescence spectroscopy data, solutions in CH₂Cl₂

Compound	Rel. intensity ^a	$\lambda_{\rm ex}{}^{b}/{\rm nm}$	$\lambda_{\rm em}^{c}/{\rm nm}$	$\phi_{ ext{PL}}{}^{d}$
A ^{8a}	High	344	422	0.604
\mathbf{B}^{8a}	High	364	422	0.794
C^{8b}	High	338	415	0.779
1A	Very low	365	460	
1B	Low	364	460	
1C	Low	362	451	
2A	Very high	290, 375	445	0.556
2B	Very high	311, 406	445	
2B (solid)	Very high	370 (sh), 414	445	
3A	High	398	461	0.565
3B	High	396	461	0.662
4A	Medium	391	460	0.738
4C	Very low	355	437	
5A	Medium	388	460	0.750
6C	Very low	351	441	
7A	Medium	394	461	0.603

^{*a*} For excitation and emission; similar experimental conditions. ^{*b*} λ_{max} for excitation. ^{*c*} λ_{max} for emission. ^{*d*} Photoluminescence quantum yield, relative to quinine sulfate (0.1 M H₂SO₄ solution) ±10%; excitation at 365 nm (see ref. 24).

 $(\lambda_{em} = 422 \text{ nm})$, **B** $(\lambda_{em} = 422 \text{ nm})$ and **C** $(\lambda_{em} = 415 \text{ nm})$ and their oxidised relatives.⁸ Complexation *via* the transition metal units, however, leads to a significant red-shift for absorption and emission that correlates well with the increased acceptor

character of the phosphorus centre and the coherent decrease of the energy of the π^* -LUMO of the dithienophospholes.^{8a} This strong red-shift for the absorption (*ca.* 20–50 nm) as well as the emission (*ca.* 25–40 nm) of all complexes presented herein, clearly rules out the existence of the free ligands in solution being responsible for the observed luminescence properties (see Fig. 4). The latter is further supported by the disappearance of the



Fig. 4 Normalised fluorescence spectra (excitation left, emission right) of A(-), $5A(\cdots)$ and 7A(--).

 $n-\pi^*$ -transition band around 290 nm in most of the complexes, which would be observed for the free ligands.¹⁹

Unfortunately, the use of the non-silyl ligand **C** in general affords transition metal functionalised materials with very poor photoluminescence properties. The same holds true for all *cis*-configured Pt-complexes whose excitation and emission (1A, 1B: $\lambda_{em} = 460$ nm; 1C: $\lambda_{em} = 451$ nm) intensities are almost negligible. This is again in contrast to the *trans*-configured Pd-complex [A]₂PdCl₂ that shows a strong photoluminescence with an emission at 470 nm when excited at its maximum wavelength for absorption (384 nm).^{8a} The latter indicates the significant influence of the complex geometry on the optoelectronic properties of the materials favouring the *trans*-configuration.

The appreciable photoluminescence properties of the rhodium (3A,B), tungsten (4A) and iron (5A, 7A) complexes based on the silyl functionalised dithienophospholes A and B, are surprisingly similar with respect to their maximum wavelengths of absorption and emission, and almost irrespective of the nature of the transition metal, the number of dithienophosphole ligands present and varying complex geometries. The complexes 3A,B, 4A, and 5A, 7A all show a maximum wavelength for their absorption at around 393 ± 5 nm with a maximum wavelength for their emission at 460/461 nm, both strongly red-shifted from the free ligands **A** and **B**, accompanied by the disappearance of the $n-\pi^*$ transition. Noteworthy differences in the spectra of the complexes, obtained under the same experimental conditions, can only be found in the relative intensities of their excitation and emission, with the rhodium-based systems 3A,B exhibiting the strongest photoluminescence.

The gold functionalised dithienophospholes 2A and 2B, on the other hand, show very intriguing optoelectronic properties with very high photoluminescence intensities, and unique wavelengths for absorption and emission indicating highly beneficial optoelectronic properties for the dithienophosphole moiety introduced by the AuCl-fragment. Although both gold complexes 2A and 2B show similar emission spectra with emissions at 445 nm, their excitation spectra differ significantly, suggesting a potential influence of the different substitution patterns of the silvl functionalities of the ligands. In contrast to the other species presented herein, 2A and 2B exhibit two significant transitions in their respective excitation spectra (see Fig. 5). The bathochromic transitions (2A: 375 nm; 2B: 405 nm) can be attributed to intraligand π - π *-transitions,⁸ whereas the hypsochromic transitions at higher energies (2A: 290 nm; 2B: 311 nm) cannot be assigned undoubtedly.¹⁹ As discussed in the literature for related gold(I) complexes, two possibilities can be considered: an intra-ligand $n-\pi^*$ -transition or a ligand to metal charge transfer process (LMCT).^{11,13} When excited at 311 nm, 2B also shows an emission at 445 nm, similar to the excitation at 406 nm (Fig. 5, middle). This feature would support the *intra*-ligand $n-\pi^*$ -transition process being responsible for the blue shifted excitation band. The excitation spectrum of 2B, however, is particularly interesting since both transitions, that are fairly narrow, are surprisingly distinct, a feature that is not commonly observed with the dithienophosphole system.⁸ This observation suggests very selective optoelectronic properties of 2B in contrast to 2A whose excitation spectrum represents a typical example for dithienophospholes (Fig. 5, top). Here, the transitions appear broader, decreasing to some extend the selectivity, allowing for an excitation over a broader range.



Fig. 5 Fluorescence spectra (excitation left, emission right) of 2A in solution, 2B in solution and 2B in the solid state.

The shifts of the absorption wavelengths for the n- π^* -/LMCT- $(\Delta \lambda = 21 \text{ nm})$ and the $\pi - \pi^*$ -transitions ($\Delta \lambda = 31 \text{ nm}$) between 2A and 2B could arise from intramolecular interactions of the gold complexes in solution that should be reduced by the sterically demanding *tert*-butyldimethylsilyl-groups in 2B, apparent in the very narrow transitions. The photoluminescence of 2B in the solid state is also extremely intense and the fluorescence spectrum also shows a maximum wavelength for emission at 445 nm, indicating that **2B** does not seem to aggregate in the solid state either (Fig. 5, bottom). The excitation spectrum, on the other hand, shows a significantly red shifted n- π^* -/LMCT-transition at 370 nm now appearing as a shoulder and a slightly shifted π - π *-transition at 414 nm. These investigations underline the intriguing properties of gold(I) functionalised dithienophospholes and indicate that the selectivity of the optoelectronic properties of the system could be significantly controlled by variation of the silyl functionality.

Concluding remarks

In conclusion we have synthesised a series of different transition metal complexes incorporating dithieno[3,2-*b*:2',3'-*d*]phosphole ligands that are accessible in high yields by chemically facile procedures. The Au- and the two W-complexes that were characterised by X-ray single crystal crystallography exhibit a high degree of π -conjugation present in the dithienophosphole ligand systems. This feature supports the potential utility of transition metal functionalised dithienophospholes for molecular electronics. The experimental data further indicate that the transition metal fragments increase the electron acceptor character of the phosphorus centre for the π -conjugated system. As a result, the energy of the π^* -LUMO of the dithienophosphole unit is significantly lowered⁸ ultimately leading to materials with smaller band gaps compared with the free ligands.

The optoelectronic properties of the complexes investigated, on the other hand, indicate that a proper choice of transition metals and respective geometries as well as suitable dithienophospholes are necessary to obtain materials with extraordinary photophysical properties that are potentially applicable in optoelectronics. Although the rhodium (3A,B), tungsten (4A) and iron (5A, 7A) complexes based on the silvl functionalised dithienophospholes A and B show appreciable photoluminescence, only the functionalisation via AuCl affords a significant optimisation of the optoelectronic properties of the dithienophosphole moiety. This strategy, however, produces highly selective materials with improved photoluminescence properties, particularly in the case of 2B, that have not been observed before with the dithienophosphole system. This functionalisation of the dithieno[3,2-b:2',3'*d*]phosphole moiety will therefore play a major role in our future investigations towards the generation of dithienophosphole-based functional materials and devices.

Experimental

General considerations

All manipulations were carried out in dry glassware and under inert atmosphere of purified argon using Schlenk techniques. Solvents were dried over appropriate drying agents and then distilled. K₂PtCl₄, W(CO)₆ and Fe₂(CO)₉ were used as received. (tht)AuCl,²⁰ [Rh(cod)Cl]₂²¹ as well as the dithienophospholes A,^{8a} \mathbf{B}^{8a} and \mathbf{C}^{8b} were prepared by literature methods. W(CO)₅·thf was generated photochemically from W(CO)₆ in thf. ¹H NMR, ¹³C NMR, and ³¹P NMR spectra were recorded on a Bruker DRX 400, Varian Mercury 200 or Unity 500 MHz-spectrometer. Chemical shifts were referenced to external 85% H₃PO₄ (³¹P) or TMS (¹³C, ¹H). Electron ionization (70 eV) mass spectra were run on a Finnigan 8230 spectrometer. IR spectra were recorded on a Nicolet Avatar 360 FT-IR Spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, Mainz.

Synthesis of $[A]_2PtCl_2$ (1A), $[B]_2PtCl_2$ (1B) and $[C]_2PtCl_2$ (1C). A solution of the respective dithienophosphole (A: 0.42 g, 1 mmol, B: 0.48 g, 1 mmol, C: 0.27 g, 1 mmol) in dichloromethane (20 mL) was treated with K_2PtCl_4 (0.21 g, 0.5 mmol) and stirred for 24 h at room temperature. Subsequently, the generated KCl was filtered off, all volatiles removed under vacuum and the residue was taken up in pentane (*ca.* 30 mL) and filtered over neutral alumina. Evaporation of the solvent provided the products as light yellow solids (**1A**: 1.04 g, 95% yield, **1B**: 1.23 g, 97% yield, **1C**: 0.78 g, 96% yield). Recrystallisation from aromatic hydrocarbons or acetonitrile, respectively, at room temperature provided yellow single crystals for all compounds.

1*A*. ³¹P{¹H} NMR (202.6 MHz, CDCl₃): δ –9.2 (d, ¹*J*(P,Pt) 3511 Hz); ¹H NMR (500 MHz, CDCl₃): δ 7.67 (dd br, ³*J*(H,P) 13.7 Hz, ³*J*(H,H) 7.6 Hz, 4H, *o*-Ph), 7.40 (t br, ³*J*(H,H) 7.5 Hz, 2H, *p*-Ph), 7.28 (t br, ³*J*(H,H) 7.6 Hz, 4H, *m*-Ph), 6.66 (br, 4H, Ar), 0.26 ppm (s, 36H; Si(CH₃)₃); ¹³C{¹H} NMR (125.0 MHz, CDCl₃): δ 149.0 (t, *J*(C,P) 6.7 Hz; Ar), 144.3 (t, *J*(C,P) 3.8 Hz; Ar), 140.0 (d br, ¹*J*(C,P) 68.0 Hz; *ipso*-Ar), 134.6 (t, *J*(C,P) 5.9 Hz; *o*-Ar), 133.0 (t, *J*(C,P) 6.7 Hz; *o*-Ar), 131.4 (s, *p*-Ph), 128.7 (t, *J*(C,P) 5.9 Hz; *m*-Ar), 128.6 (d, ¹*J*(C,P) 101.6 Hz; *ipso*-Ph), -0.1 ppm (s; SiC₃). Calc. for C₄₀H₅₀Cl₂P₂PtS₄Si₄ (1097.04): C, 43.70; H, 4.58; S, 11.67. Found: C, 43.65; H, 4.48; S, 11.63%.

1B. ³¹P{¹H} NMR (202.6 MHz, CDCl₃): δ –10.5 (d, ¹*J*(P,Pt) 3508 Hz); ¹H NMR (500 MHz, CDCl₃): δ 7.70 (dd br, ³*J*(H,P) 14.3 Hz, ³*J*(H,H) 7.6 Hz, 4H, *o*-Ph), 7.39 (t br, ³*J*(H,H) 7.5 Hz, 2H, *p*-Ph), 7.27 (t br, ³*J*(H,H) 7.6 Hz, 4H, *m*-Ph), 6.69 (br, 4H, Ar), 0.83 (s, 36H, SiC(CH₃)₃), 0.20 (s, 12H, Si(CH₃)₂), 0.18 (s, 12H, Si(CH₃)₂); ¹³C{¹H} NMR (125.0 MHz, CDCl₃): δ 149.1 (t, *J*(C,P) 6.9 Hz; Ar), 141.3 (t, *J*(C,P) 5.2 Hz; Ar), 140.5 (d br, ¹*J*(C,P) 69.4 Hz; *ipso*-Ar), 135.9 (t, *J*(C,P) 7.2 Hz; *o*-Ar), 133.2 (t, *J*(C,P) 6.2 Hz; *o*-Ar), 131.6 (s, *p*-Ph), 128.7 (t, *J*(C,P) 5.9 Hz; *m*-Ar), 128.6 (d, ¹*J*(C,P) 101.5 Hz; *ipso*-Ph), 26.3 (s; SiC(CH₃)₃), 16.9 (s; SiC(CH₃)₃), -4.9 ppm (s; SiMe₂), -5.0 ppm (s; SiMe₂). Calc. for C₅₂H₇₄Cl₂P₂PtS₄Si₄ (1265.23): C, 49.27; H, 5.88; S, 10.12. Found: C, 49.03; H, 5.87; S, 10.21%.

IC. ³¹P{¹H} NMR (80.9 MHz, CD₂Cl₂): δ -7.6 (d, ¹*J*(P,Pt) = 3506 Hz); ¹H NMR (500 MHz, CD₂Cl₂): δ 7.53 (dd br, ³*J*(H,P) 12.5 Hz, ³*J*(H,H) 7.8 Hz, 4H, *o*-Ph), 7.40 (t br, ³*J*(H,H) 7.8 Hz, 2H, *p*-Ph), 7.30 (m br, ³*J*(H,H) 7.8 Hz, 4H, *m*-Ph), 7.20 (dd br, ³*J*(H,H) 5.0 Hz, ⁴*J*(H,P) 2.6 Hz, 4H, Ar–H), 6.77 (d br, ³*J*(H,P) 5.0 Hz, 4H, Ar–H); ¹³C{¹H} NMR (125.0 MHz, CD₂Cl₂): δ 148.7 (pt, ¹³*J*(C,P) 8.9 Hz, *ipso*-Ar), 144.9 (pt, ²*J*(C,P) 5.5 Hz, Ar), 137.7 (d br, ¹*J*(C,P) 49.9 Hz, *ipso*-Ph), 132.6 (pt, ^{2/4}*J*(C,P) 5.6 Hz, *o*-Ar), 131.8 (s br, *p*-Ph), 129.0 (pt, ^{3/5}*J*(C,P) 6.7 Hz, *m*-Ar), 128.3 (pt, ^{3/5}*J*(C,P) 6.7 Hz, *m*-Ar), 127.8 (pt, ^{2/4}*J*(C,P) 6.7 Hz, *o*-Ar). Calc. for C₂₈H₁₈Cl₂P₂PtS₄, ¹/₂CH₂Cl₂ (853.10): C, 40.12; H, 2.24; S, 15.03. Found: C, 40.29; H, 2.33; S, 14.92%.

Synthesis of [A]AuCl (2A) and [B]AuCl (2B). A solution of the respective dithienophosphole (A: 0.42 g, 1 mmol, B: 0.48 g, 1 mmol) in dichloromethane (20 mL) was treated with (tht)AuCl (0.32 g, 1 mmol), dissolved in CH_2Cl_2 (5 mL) and stirred for 1 h at room temperature. Subsequently, all volatiles were removed under vacuum and the residue was taken up in pentane (*ca.* 10 mL). The gold complexes 2A and 2B were obtained as colourless or light yellow crystals from concentrated pentane solutions kept at 4 °C (2A: 0.53 g, 90% yield, 2B: 0.62 g, 84% yield).

2*A*. ³¹P{¹H} NMR (202.6 MHz, CDCl₃): δ 1.9; ¹H NMR (500 MHz, CDCl₃): δ 7.62 (dd, ³*J*(H,P) 15.0 Hz, ³*J*(H,H) 7.9 Hz, 2H, *o*-Ph), 7.38 (tm, ³*J*(H,H) 7.9 Hz, 1H, *p*-Ph), 7.28 (td, ³*J*(H,H) 7.9 Hz, ⁴*J*(H,P) 3.1 Hz, 2H, *m*-Ph), 7.20 (d, ³*J*(H,P) 2.1 Hz, 2H, Ar), 0.35 (s, 18H, Si(CH₃)₃); ¹³C{¹H} NMR (125.0 MHz, CDCl₃): δ 150.0 (d, *J*(C,P) 17.2 Hz, Ar), 146.2 (d, *J*(C,P) 9.7 Hz, Ar),

139.6 (d, J(C,P) 65.5 Hz, *ipso*-Ar), 133.6 (d, ${}^{2}J(C,P)$ 17.2 Hz, Ar), 132.5 (br, *p*-Ph), 132.4 (d, ${}^{2}J(C,P)$ 16.1 Hz, *o*-Ar), 129.4 (d, ${}^{3}J(C,P)$ 11.8 Hz, *m*-Ph), 126.6 (d, J(C,P) 61.2 Hz, *ipso*-Ph), -0.2 (s, SiC₃). Calc. for C₂₀H₂₅AuClPS₂Si₂ (648.00): C, 37.01; H, 3.88; S, 9.88. Found: C, 36.90; H, 3.72; S, 9.71%.

2B. ³¹P{¹H} NMR (202.6 MHz, CDCl₃): δ 2.1; ¹H NMR (500 MHz, CDCl₃): δ 7.62 (dd, ³*J*(H,P) 14.3 Hz, ³*J*(H,H) 7.6 Hz, 2H, *o*-Ph), 7.38 (tm, ³*J*(H,H) 7.6 Hz, 1H, *p*-Ph), 7.28 (td, ³*J*(H,H) 7.6 Hz, ⁴*J*(H,P) 2.8 Hz, 2H, *m*-Ph), 7.20 (d, ³*J*(H,P) 1.5 Hz, 2H, Ar), 0.93 (s, 18H, SiC(CH₃)₃), 0.31 (s, 6H, Si(CH₃)₂), 0.30 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (125.0 MHz, CDCl₃): δ 150.1 (d, *J*(C,P) 14.4 Hz, Ar), 143.3 (d, *J*(C,P) 9.6 Hz, Ar), 139.3 (d, *J*(C,P) 67.1 Hz, *ipso*-Ar), 132.5 (br, *p*-Ph), 129.4 (d, ³*J*(C,P) 13.4 Hz, *m*-Ph), 126.6 (d, *J*(C,P) 60.4 Hz, *ipso*-Ph), 26.3 (s; SiC(CH₃)₃), 16.8 (s; SiC(CH₃)₃), -4.9 ppm (s; SiMe₂), -5.0 ppm (s; SiMe₂). Calc. for C₂₆H₃₇AuCIPS₂Si₂ (732.10): C, 42.59; H, 5.09; S, 8.75. Found: C, 42.53; H, 5.01; S, 8.68%.

Synthesis of [A]Rh(cod)Cl (3A) and [B]Rh(cod)Cl (3B). A solution of the respective dithienophosphole (A: 0.42 g, 1 mmol, **B**: 0.48 g, 1 mmol) in thf (20 mL) was treated with $[Rh(cod)Cl]_2$ (0.25 g, 0.5 mmol) and stirred for 30 min at room temperature. Subsequently, all volatiles were removed under vacuum and the residue was taken up in pentane (*ca.* 10 mL) and filtered over neutral alumina. The rhodium complexes **3A** and **3B** were obtained as orange solids from concentrated pentane solutions kept at $-30 \,^{\circ}$ C (**3A**: 0.48 g, 73% yield, **3B**: 0.57 g, 77% yield).

34. ³¹P{¹H} NMR (202.6 MHz, CDCl₃): δ 11.5 (d, ¹*J*(P,Rh) 148.3 Hz); ¹H NMR (500 MHz, CDCl₃): δ 7.77 (dd, ³*J*(H,P) 11.9 Hz, ³*J*(H,H) 7.6 Hz, 2H, *o*-Ph), 7.39 (s, 2H, Ar), 7.34 (m, 3H, Ph), 5.56 (br, 2H, CH of cod), 3.71 (br, 2H, CH of cod), 2.40 (d br, *J* 10.1 Hz, 2H CH₂ of cod), 2.06 (d br, *J* 13.4 Hz, 2H, CH₂ of cod), 0.32 (s, 18H, Si(CH₃)₃); ¹³C{¹H} NMR (125.0 MHz, CDCl₃): δ 148.0 (d, *J*(C,P) 13.0 Hz, Ar), 143.6 (d, *J*(C,P) 8.0 Hz, Ar), 142.8 (d, ¹*J*(C,P) 44.8 Hz, *ipso*-Ar), 134.2 (d, ²*J*(C,P) 13.0 Hz, Ar), 133.5 (d, ²*J*(C,P) 14.0 Hz, *o*-Ar), 130.6 (d, ¹*J*(C,P) 41.9 Hz, *ipso*-Ph), 130.4 (br, *p*-Ph), 128.6 (d, ³*J*(C,P) 11.0 Hz, *m*-Ph), 106.1 (dd, ¹*J*(C,Rh) 13.0 Hz, ²*J*(C,P) 7.0 Hz, CH of cod), 69.6 (d, ¹*J*(C,Rh) 13.0 Hz, CH of cod), 33.4 (s, CH₂ of cod), 28.8 (s, CH₂ of cod), -0.0 (s, SiC₃). Calc. for C₂₈H₃₇ClPRhS₂Si₂ (663.23): C, 50.71; H, 5.62; S, 9.67. Found: C, 50.63; H, 5.58; S, 9.71%.

3B. ${}^{31}P{}^{1}H{}$ NMR (202.6 MHz, CDCl₃): δ 10.6 (d, ${}^{1}J(P,Rh)$ 148.3 Hz); ¹H NMR (500 MHz, CDCl₃): δ 7.78 (dd, ³J(H,P) 11.6 Hz, ³J(H,H) 7.6 Hz, 2H, o-Ph), 7.41 (s, 2H, Ar), 7.33 (m, 3H, Ph), 5.54 (br, 2H, CH of cod), 3.68 (br, 2H, CH of cod), 2.37 (br, 2H CH₂ of cod), 2.05 (br, 2H, CH₂ of cod), 0.91 (s, 18H, SiC(CH₃)₃), 0.31 (s, 6H, Si(CH₃)₂), 0.29 (s, 6H, Si(CH₃)₂); ¹³C{¹H} NMR (125.0 MHz, CDCl₃): δ 148.0 (d, J(C,P) 9.7 Hz, Ar), 142.7 (d, ¹J(C,P) 43.0 Hz, ipso-Ar), 140.6 (d, J(C,P) 6.4 Hz, Ar), 135.5 (d, ²J(C,P) 11.8 Hz, Ar), 133.4 (d, ²J(C,P) 14.0 Hz, o-Ar), 130.4 (d, ¹J(C,P) 41.9 Hz, ipso-Ph), 130.3 (br, p-Ph), 128.5 (d, ³*J*(C,P) 10.7 Hz, *m*-Ph), 105.9 (dd, ¹*J*(C,Rh) 12.9 Hz, ²*J*(C,P) 7.5 Hz, CH of cod), 69.7 (d, ¹J(C,Rh) 12.9 Hz, CH of cod), 33.3 (s, CH₂ of cod), 28.8 (s, CH₂ of cod), 26.3 (s; SiC(CH₃)₃), 17.0 (s; $SiC(CH_3)_3$, -4.9 ppm (s; $SiMe_2$), -5.0 ppm (s; $SiMe_2$). Calc. for C₃₄H₄₉ClPRhS₂Si₂ (746.13): C, 54.64; H, 6.61; S, 8.58. Found: C, 55.00; H, 6.82; S, 8.60%.

Synthesis of [A]W(CO)₅ (4A) and [C]W(CO)₅ (4C). A solution of the respective dithienophosphole (A: 0.83 g, 2 mmol, C: 0.52 g, 2 mmol) in THF (10 mL) was treated with W(CO)₅ thf (0.87 g, 2.2 mmol) dissolved in thf (20 ml) at room temperature. The reaction mixture was stirred for 16 h, all volatile materials were then removed under vacuum. The light yellow or off white residue, respectively, was taken up in hexane (*ca.* 10 ml). The product 4A was obtained from a concentrated hexane–toluene (1 : 1) solution at -30 °C as yellow crystals (0.76 g, 51% yield); complex 4C was obtained from a concentrated hexane solution at -30 °C as off white powder (1.07 g, 83% yield).

4*A*. ³¹P{¹H} NMR (162.0 MHz, CDCl₃): δ –7.9 (¹*J*(P,W) 227.9 Hz); ¹H NMR (400 MHz, CDCl₃): δ 7.51 (m br, 2H, *o*-Ph), 7.37 (m br, 5H, Ar–H), 7.31 (m br, 2H, Ar–H), 0.32 (s, 18H, Si(CH₃)₃); ¹³C{¹H} NMR (100.4 MHz, CDCl₃): δ 198.4 (d, ²*J*(C,P) 20.7 Hz, ¹*J*(C,W) 406.5 Hz, *trans*-CO), 195.8 (d, ²*J*(C,P) 6.8 Hz, ¹*J*(C,W) 137.9 Hz, *cis*-CO), 146.8 (d, ²*J*(C,P) 38.9 Hz, Ar), 146.5 (d, *J*(C,P) 2.9 Hz, Ar), 144.8 (d, *J*(C,P) 7.8 Hz, Ar), 132.7 (d, ¹*J*(C,P) 40.2 Hz, *ipso*-Ph), 132.0 (d, ²*J*(C,P) 15.3 Hz, *o*-Ar), 130.6 (d, ²*J*(C,P) 13.3 Hz, *o*-Ar), 130.3 (d, ⁴*J*(C,P) 2.0 Hz, *p*-Ph), 128.8 (d, ³*J*(C,P) 10.7 Hz, *m*-Ar), -0.3 (s, SiC₃). IR (KBr, cm⁻¹): 2071, 1989(sh), 1958, 1941, 1905 *v*(CO). MS (70 eV): *m*/*z* (relative intensity) 740 (20) [M⁺], 684 (30) [M⁺ - 2CO], 600 (130) [M⁺ - 5CO], 432 (40) [PhPW(CO)₅⁺], 73 (100) [SiMe₃⁺]. Calc. for C₂₅H₂₅O₅PS₂Si₂W (739.99): C, 40.54; H, 3.40; S, 8.66. Found: C, 40.76; H, 3.59; S, 8.66%.

4C. ³¹P{¹H} NMR (162.0 MHz, CDCl₃): δ −3.9 (¹*J*(P,W) 230.0 Hz); ¹H NMR (400 MHz, CDCl₃): δ 7.48 (m br, 2H, *o*-Ph), 7.36 (m br, 3H, Ar–H), 7.29 (dd, *J* 4.8 Hz, *J* 0.6 Hz, 2H, Ar–H); ¹³C{¹H} NMR (100.4 MHz, CDCl₃): δ 198.0 (d, ¹*J*(C,W) 21.0 Hz, *trans*-CO), 195.6 (d, ²*J*(C,P) 6.5 Hz, ¹*J*(C,W) 406.5 Hz, *cis*-CO), 144.8 (d, ¹*J*(C,P) 47.7 Hz, *ipso*-Ar), 141.7 (br, Ar), 132.5 (d, ¹*J*(C,P) 40.2 Hz, *ipso*-Ph), 130.4 (d, ²*J*(C,P) 13.2 Hz, *o*-Ar), 130.4 (d, ⁴*J*(C,P) 2.0 Hz, *p*-Ph), 128.4 (d, ³*J*(C,P) 10.7 Hz, *m*-Ar), 127.7 (d, ³*J*(C,P) 11.2 Hz, *m*-Ar), 130.4 (d, ²*J*(C,P) 16.7 Hz, *o*-Ar). IR (KBr, cm⁻¹): 2073, 2019, 1990, 1945, 1917 *v*(CO). MS (70 eV): *m*/*z* (relative intensity) 596 (40) [M⁺], 540 (25) [M⁺ – 2CO], 512 (40) [M⁺ – 3CO], 456 (100) [M⁺ – 5CO]. Calc. for C₁₉H₉O₅PS₂W (644.01): C, 38.28; H, 1.52; S, 10.76. Found: C, 38.37; H, 1.62; S, 10.88%.

Synthesis of $[A]Fe(CO)_4$ (5A). A solution of $Fe_2(CO)_9$ (0.41 g, 1.1 mmol) in THF (30 mL) was treated with dithienophosphole A (0.42 g, 1.0 mmol), dissolved in THF (10 mL) at room temperature and stirred for 1 h. The volatiles were removed under vacuum and the residue taken up in hexane (*ca.* 30 mL). Filtration over neutral alumina provides 5A as red oil in 85% yield (0.50 g).

³¹P{¹H} NMR (162.0 MHz, CDCl₃): δ 49.9; ¹H NMR (400 MHz, CDCl₃): δ 7.62 (dd, J 12.74 Hz, J 6.74 Hz, 2H, *o*-Ph), 7.38 (m br, 3H, Ar), 7.28 (br, 2H, *m*-Ph), 0.34 (s, 18H, Si(CH₃)₃); ¹³C{¹H} NMR (100.4 MHz, CDCl₃): δ 212.5 (d, ²J(C,P) 20.2 Hz, CO), 146.7 (d, J(C,P) 11.7 Hz, Ar), 146.7 (d, J(C,P) 52.7 Hz, *ipso*-Ar), 145.4 (d, J(C,P) 8.6 Hz, Ar), 131.8 (d, ²J(C,P) 14.4 Hz, Ar), 131.5 (d, ²J(C,P) 12.3 Hz, *o*-Ar), 131.0 (br, *p*-Ph), 130.8 (d, J(C,P) = 46.8 Hz, *ipso*-Ar), 128.7 (d, ³J(C,P) 11.2 Hz, *m*-Ph), -0.3 (s, SiC₃). IR (KBr, cm⁻¹): 2051, 1977, 1947, 1933 ν (CO). Calc. for C₂₄H₂₅FeO₄PS₂Si₂ (583.98): C, 49.31; H, 4.31; S, 10.97. Found: C, 49.39; H, 4.29; S, 10.87%.

Synthesis of $[C]_2W(CO)_4$ (6C). A solution of $[C]W(CO)_5$ (4C, 0.64 g, 1 mmol) in THF (10 mL) was treated with another equivalent of the dithienophosphole C (0.26 g, 1 mmol) dissolved in thf (20 ml) at room temperature. The reaction mixture was then stirred for 4 h at room temperature under irradiation with UV-light, before all volatile materials were removed under vacuum. Complex 6C was obtained from a hexane–toluene (1 : 1) solution at -30 °C as yellow crystals (0.59 g, 67% yield).

³¹P{¹H} NMR (202.6 MHz, CDCl₃): δ –2.4 (¹*J*(P,W) 225.0 Hz); ¹H NMR (500 MHz, CDCl₃): δ 7.28 (m br, 4H, *o*-Ph), 7.21 (m br, 6H, Ph–H), 7.09 (dd, ³*J*(H,H) 5.0 Hz, ³*J*(H,P) 2.8 Hz, 4H, Ar–H), 7.00 (d, ³*J*(H,H) 5.0 Hz, 4H, Ar–H); ¹³C{¹H} NMR (100.4 MHz, CDCl₃): δ 202.9 (pt, ²*J*(C,P) 8.6 Hz, CO), 200.7 (t, ²*J*(C,P) 7.8 Hz, CO), 143.6 (dd, ¹*J*(C,P) 43.5 Hz, ³*J*(C,P) 4.5 Hz, *ipso*-Ar), 141.5 (pt, ²*J*(C,P) 3.7 Hz, Ar), 135.9 (d br, ¹*J*(C,P) 47.8 Hz, *ipso*-Ph), 129.7 (pt, ^{2/4}*J*(C,P) 6.2 Hz, *o*-Ar), 129.2 (s br, *p*-Ph), 128.3 (pt, ^{3/5}*J*(C,P) 5.0 Hz, *m*-Ar), 126.6 (pt, ^{3/5}*J*(C,P) 5.1 Hz, *m*-Ar), 125.6 (pt, ^{2/4}*J*(C,P) 8.2 Hz, *o*-Ar). IR (KBr, cm⁻¹): 2016, 1921, 1907, 1884, 1865 *v*(CO). Calc. for C₃₂H₁₈O₄P₂S₄W (839.91): C, 45.73; H, 2.16; S, 15.26. Found: C, 45.74; H, 2.17; S, 15.23%.

Synthesis of $[A]_2$ Fe(CO)₃ (7A). A solution of Fe₂(CO)₉ (0.27 g, 0.75 mmol) in THF (25 mL) was treated with dithienophosphole A (0.62 g, 1.5 mmol), dissolved in THF (10 mL) at room temperature and stirred for 4 h under irradiation with UV-light. The volatiles were then removed under vacuum and the residue taken up in pentane (*ca.* 40 mL). Filtration over neutral alumina provides **7A** as yellow solid in 87% yield (0.64 g).

³¹P{¹H} NMR (162.0 MHz, CDCl₃): δ 59.4; ¹H NMR (400 MHz, CDCl₃): δ 7.65 (br, 4H, *o*-Ph), 7.32 (m br, 10H, Ar), 0.30 (s, 36H, Si(CH₃)₃); ¹³C{¹H} NMR (100.4 MHz, CDCl₃): δ 212.7 (t, ²*J*(C,P) 29.7 Hz, CO), 149.0 (m, *ipso*-Ar), 145.9 (t, *J*(C,P) 5.2 Hz, Ar), 143.8 (t, ¹*J*(C,P) 3.4 Hz, Ar), 133.9 (m, *ipso*-Ar), 132.7 (d, *J*(C,P) 6.9 Hz, Ar), 131.4 (t, *J*(C,P) 6.1 Hz, Ar), 129.8 (s, *p*-Ph), 128.3 (t, *J*(C,P) 5.2 Hz, *m*-Ph), -0.2 (s, SiC₃). IR (KBr, cm⁻¹): 1905, 1884 ν (CO). Calc. for C₄₃H₅₀FeO₃P₂S₄Si₄ (972.05): C, 53.07; H, 5.18; S, 13.18. Found: C, 53.01; H, 5.25; S, 13.28%.

X-Ray crystallography

Crystallographic data for **2B**, **4A** and **6C** are summarised in Table 1. For all complexes studied, data were collected on a Bruker SMART D8 goniometer with APEX CCD detector at 110 K using Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator). The unit cell parameters were obtained by the least-squares refinement of 6172 (**2B**), 8006 (**4A**) or 986 (**6C**) reflections, respectively. SADABS²² method of correcting absorption was applied in all cases. The structures were solved by direct methods (SHELXTL)²³ and refined on F^2 by full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined using a riding model.

CCDC reference numbers 276963 (4A), 276964 (2B), 276965 (6C).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509277a

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