Synthesis, characterization, and coordination chemistry of phosphines with ethylenedioxythiophene substituents

M'hamed Chahma, Daniel J.T. Myles, and Robin G. Hicks

Abstract: The preparation of several new phosphines bearing one or more 3,4-ethylenedioxythiophene (EDOT) units as substituents linked at the 2-thienyl position is described. The phosphines were prepared by reaction of lithiated EDOT intermediates with appropriate chlorophosphines to afford (3,4-ethylenedioxy-2-thienyl)diphenylphosphine (**1**), (bis(3,4-ethylenedioxy-2-thienyl)phenylphosphine (**2**), tris(3,4-ethylenedioxy-2-thienyl)phosphine (**3**), 2,5-bis(diphenylphosphino)-3,4-ethylenedioxythiophene (**4**), and 2-diphenylphosphino-5-mesitylthio-3,4-ethylenedioxythiophene (**5**). Molybdenum carbonyl complexes of compounds **1**–**3** were prepared by reaction of the phosphine ligands with *cis*-$Mo(CO)_4(pip)_2$. In all cases, spectroscopic evidence is fully consistent with the phosphines acting as monodentate, P-bound ligands. Electrochemical studies on the phosphines as well as their metal complexes indicate that the normal electrochemical redox robustness of the EDOT group is dramatically decreased by the presence of phosphine substituents: all compounds exhibited irreversible oxidation processes and no evidence of electropolymerization was observed for the phosphines bearing two or three EDOT groups.

Key words: phosphines, thiophene, 3,4-ethylenedioxythiophene, EDOT, electrochemistry, coordination complexes.

Résumé : On décrit la préparation de plusieurs nouvelles phosphines portant un ou plusieurs unités de 3,4-éthylènedioxythiophène (EDOT) comme substituants liés à la position 2-thiényle. On a préparé les phosphines par la réaction d'intermédiaires EDOT lithiés avec les chlorophosphines appropriées qui ont conduit à la formation des (3,4-éthylènedioxy-2-thiényl)diphénylphosphine (**1**), bis(3,4-éthylènedioxy-2-thiényl)phénylphosphine (**2**), tris(3,4-éthylènedioxy-2-thiényl)phosphine (**3**), 2,5-bis(diphénylphosphino)-3,4-éthylènedioxythiophène (**4**) et 2-diphénylphosphino-5-mésitylthio-3,4-éthylènedioxythiophène (**5**). La réaction des ligands phosphines avec les *cis*-$Mo(CO)_4(pip)_2$ a permis de préparer les complexes du molybdène carbonyle des composés **1**–**3**. Dans tous les cas, les données spectroscopiques sont en total accord avec le fait que les phosphines agissent comme des ligands monodentates liés par le phosphore. Des études électrochimiques sur les phosphines ainsi que sur leurs complexes métalliques indiquent que la solidité redox électrochimique normale du groupe EDOT est dramatiquement abaissée par la présence des substituants phosphines : tous les composés donnent lieu à des processus d'oxydation irréversibles et aucune électropolymérisation n'a été observée avec les phosphines portant deux ou trois groupes EDOT.

Mots clés : phosphines, thiophène, 3,4-éthylènedioxythiophène, EDOT, électrochimie, complexes de coordination.

[Traduit par la Rédaction]

Introduction

The importance of phosphine ligands in (organo)transition metal chemistry cannot be overstated. The ability to modulate steric and electronic properties of phosphines (1) and their resulting metal complexes has facilitated the development of metal phosphine-based catalysis in a wide range of forums, particularly in late metal-catalyzed cross-coupling reactions (Suzuki, Stille, Kumada–Corriu, etc.) (2). As one of the prototypical members of this ligand class, triphenylphosphine is a true benchmark ligand. In recent years, other arylphosphine derivatives have been explored in which some or all of the phenyl groups have been replaced by heteroaromatic rings such as pyridine (3) and furan (4). Phosphines containing thiophene subtitutents have also received attention. Although they typically behave as simple P-monodentate ligands (5), thienylphosphines can also act as bridging ligands via the thiophene sulfur atom (6), or as chelating ligands involving cyclometallation of one of the thiophene rings (7).

Thienylphosphine complexes have also attracted interest because of the possibility of making phosphine-substituted conjugated polythiophenes in which the electronic properties of the polymer can be tuned via metal coordination at the phosphine (8). Metal–organic polymers have received a great deal of interest stemming from the potential properties that may arise from polymers containing both organic and inorganic elements (9). There has been a particularly strong emphasis on polymers containing metals as part of, or attached to, conjugated frameworks (10). The main motivation behind

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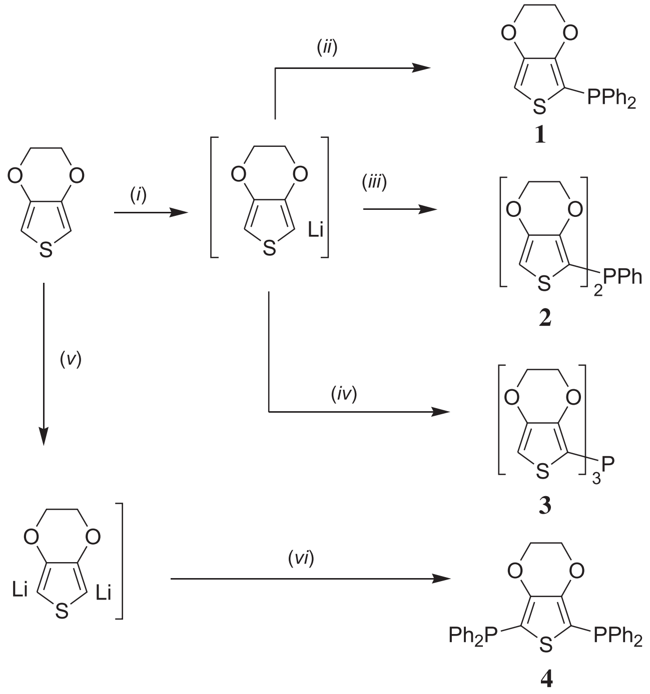
Scheme 1.



these studies is to explore the possibilities of making new materials, which combine inherent functional properties of purely organic conjugated polymers (11) such as conductivity, electrochromism, and light emission with the electronically interesting features of metal complexes (magnetic, optical, etc.).

Among the many thiophenes that have been incorporated into conjugated organic polymers, 3,4-ethylendioxythiophene (EDOT) stands out as an electron-rich derivative. The strongly electron-donating oxygen atoms render EDOT relatively easily oxidized and impart exceptional stability to the resulting homopolymer. The outstanding properties of poly(EDOT) have led to the synthesis and study of a wide range of hybrid materials of EDOT with other organic and inorganic moieties (12). However, no EDOT-substituted phosphines have been reported. It occurred to us that such species should be useful ligands and may lead to interesting materials from hybrid EDOT–phosphine–metal complexes and polymers. To this end, herein we describe the synthesis, characterization, and preliminary coordination chemistry of triarylphosphine derivatives bearing 3,4-ethylenedioxy-2-thienyl groups as substituents.

Synthesis and characterization of EDOT phosphines

The EDOT–phosphine derivatives were prepared by reactions of in-situ-generated, lithiated EDOT compounds with the appropriate chlorophosphine (Scheme 1). Thus, Li$^+$EDOT$^-$ reacts with chlorodiphenylphosphine, dichlorophenylphosphine, and trichlorophosphine to give $Ph_2P(EDOT)$ (**1**), $PhP(EDOT)_2$ (**2**), and $P(EDOT)_3$ (**3**), respectively. In addition, 2,5-bis(diphenylphosphino)-3,4-ethylenedioxythiophene (Ph_2P-EDOT-PPh_2) (**4**) was prepared by reaction of chlorodiphenylphosphine with doubly lithiated EDOT.

Scheme 2.

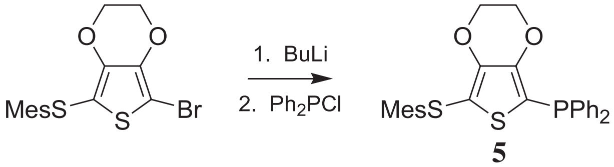


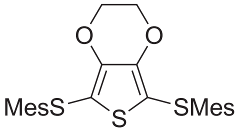
Table 1. Characterization data for EDOT–phosphines **1**–**5** and related compounds.

Compound	λ_{max} (nm)	^{31}P NMR δ (ppm)	E_p (V vs. Fc/Fc$^+$)
EDOT	260	—	+0.93
EDOT–PPh_2 (**1**)	274	–28.1	+0.79
$(EDOT)_2PPh$ (**2**)	274	–50.5	+0.68
$(EDOT)_3P$ (**3**)	277	–68.5	+0.60
Ph_2P-EDOT-PPh_2 (**4**)	292	–26.5	+0.52
MesS-EDOT-PPh_2 (**5**)	288, 305	–27.6	+0.57
MesS-EDOT-SMes (**6**)	305	—	+0.40[a]

[a] Reversible.

In addition to compounds **1**–**4**, an EDOT derivative with one diphenylphosphine (Ph_2P) and one mesitylthio (MesS) substituent was prepared for comparison of electrochemical properties. Compound **5** was synthesized from 5-bromo-2-(mesitylthio)-3,4-ethylenedioxythiophene) (13) via lithium–halogen exchange followed by treatment with Ph_2PCl using analogous protocols employed in the synthesis of **1**–**4**. (Scheme 2).

Although some EDOT derivatives with unsubstituted thiophene α-carbon atoms are unstable to air and moisture, all of the EDOT phosphines are air-stable compounds. Table 1 summarizes pertinent physicochemical data for the new EDOT-substituted phosphines as well as EDOT itself and 2,5-bis(mesitylthio)3,4-ethylenedioxythiophene (**6**), a disubstituted EDOT derivative previously made in our lab.(13) The UV–vis spectra all have lowest energy absorption maxima in the neighborhood of 277–290 nm. These are all slightly red-shifted relative to EDOT itself (λmax = 260 nm) indicative of a weak electronic perturbation of the EDOT chromophore by the phosphine moieties. The ^{31}P NMR chemical shifts of the series $(EDOT)_nPPh_{3-n}$ progress smoothly to more negative values as phenyl groups are successively replaced by more electron-rich EDOT moieties. Analogous behaviour is observed in the related series of unsubstituted 2-thienyl–phenylphosphines $(2\text{-Th})_nPPh_{3-n}$ (Fig. 1) (6*a*). Similar trends can also be found in triarylphosphines bearing para substituents, for which the more electron-donating groups give rise to more negative δ ^{31}P NMR values (14).



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The redox properties of compounds **1**–**5** were examined by cyclic voltammetry. All new compounds **1**–**5** exhibited irreversible oxidation waves at the potentials given in Table 1.

Table 2. Characterization data for Mo complexes of EDOT phosphines and related compounds.

Compound	^{31}P NMR δ (ppm)	ν(CO) (cm^{-1})	E_p (V vs. Fc/Fc$^+$)
cis-$\mathrm{Mo(CO)_4(EPPh_2)_2}$ (**7**)	+24.3	2023m, 1924s, 1908s, 1878m	+0.32
$\mathrm{Mo(CO)_5(E_2PPh)}$ (**8**)	+7.6	1992w, 1946sh	+0.67
$\mathrm{Mo(CO)_5(E_3P)}$ (**9**)	–8.5	1990w, 1947sh	+0.69
cis-$\mathrm{Mo(CO)_4(ThPPh_2)_2}$[6c]	+26.7	2010, 1900, 1880	—
$\mathrm{Mo(CO)_5(Th_2PPh)}$[6c]	+15.0	2020, 1945, 1905, 1885	—
$\mathrm{Mo(CO)_5(Th_3P)}$[6c]	+6.6	2020, 1945, 1910, 1890	—

Fig. 1. ^{31}P NMR chemical shifts for (2-thienyl)phenylphosphines (data from ref. 14) and (3,4-ethylenedioxy-2-thienyl)phenylphosphines.

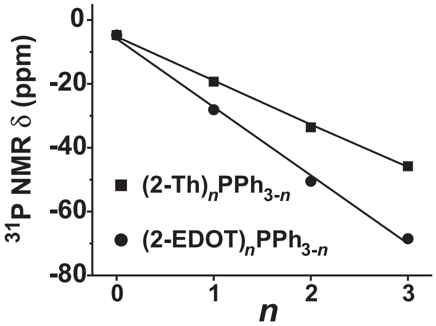
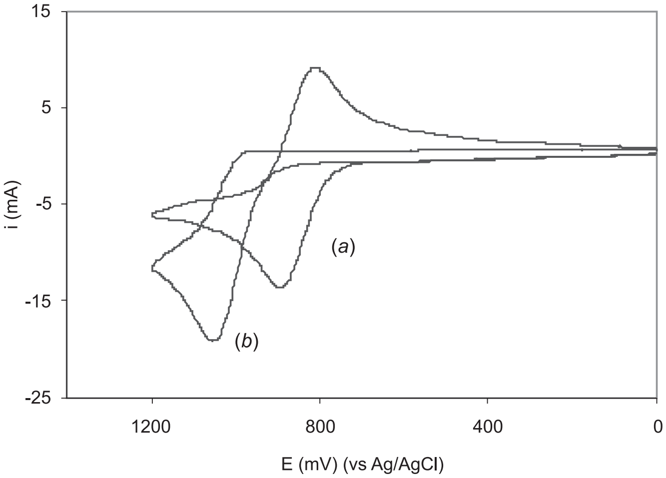


Fig. 2. CV of 2 × 10^{-4} mol/L of **6** (*a*) alone and (*b*) with 1 equiv. of $\mathrm{Ph_3P}$ added.



For compounds **1**–**3**, the irreversible nature of the oxidation was not unexpected because the EDOT groups in these compounds contain unsubstituted positions on the thiophene ring. These unsubstituted positions are known to be highly reactive sites in oxidized thiophenes. However, the bis(phosphine)-substituted EDOT **4** and 5-mesitylthio-2-diphenylphosphine-3,4-ethylenedioxythiohene (**5**) also exhibited irreversible behaviour upon oxidation. Thiophenes containing substituents at all the 2 (or 5) positions generally can be electrochemically oxidized to give radical cations that are stable at least on electrochemical timescales, For example, bis(mesitylthio)EDOT **6** undergoes a fully reversible oxidation to its radical cation at +0.40 mV. Evidently, the presence of a phosphine group on one of the a carbon atoms of EDOT render the oxidation of the latter moiety irreversible. In general, the oxidation of thiophene derivatives bearing two or more unsubstituted α-carbon atoms are irreversibly oxidized because the resulting radical cations couple at these carbons — this is the first step in the electropolymerization of thiophene and its derivatives. The source of instability in compounds **1**–**5** appears to arise from reactions specific to phosphine-containing thiophenes: although, in principle, compounds **2** and **3** could lead to poly(thiophene–phosphine) materials upon oxidation, repeated electrochemical cycling lead to passivation of the electrode and no formation of polymer was observed. Similar behavior was observed in related phosphinoterthiophenes (8*e*). As a final piece of supporting evidence, the reversibility of the electrochemical oxidation of **6** is dramatically decreased upon addition of triphenylphosphine (Fig. 2).

Coordination complexes

Preliminary investigations into the coordination chemistry of the phosphines involved reactions with molybdenum carbonyl species; related complexes of other 2-thienylphosphines have been reported (6*b*, 6*c*, 6*f*). Reactions of **1** with the reagent *cis*-$\mathrm{Mo(CO)_4(piperidine)_2}$ (15) led to the expected cis-disubstituted product *cis*-$\mathrm{Mo(CO)_4(EPPh_2)_2}$ (**7**). However, reactions of **2** or **3** with *cis*-$\mathrm{Mo(CO)_4(piperidine)_2}$ in a 2:1 ratio did gave mixtures of products, which appeared to contain the *mono*substituted products $\mathrm{Mo(CO)_5(PAr_3)}$ in addition to the anticipated disubstituted products. Changing the stoichiometric ratio of phosphines to Mo to 1:1 produced the monosubstituted products **8** and **9** in high yields. These unexpected products must result from intermolecular CO transfer and may be a consequence of the larger steric bulk of the phosphines bearing multiple EDOT substituents. The qualitative similarity of an EDOT group to a naphthyl group would lead to approximately similar steric features between $\mathrm{(EDOT)_3P}$ (**3**) and tris(1-naphthyl)phosphine, the latter of which has a cone angle of ~200° (1*c*).

$$cis\text{-}\mathrm{Mo(CO)_4}(PAr_3)_2 \xleftarrow{\mathbf{1}} cis\text{-}\mathrm{Mo(CO)_4(pip)_2} \xrightarrow{\mathbf{2}\text{ or }\mathbf{3}} \mathrm{Mo(CO)_5}(PAr_3)$$

7 PAr_3 = **1**
8 PAr_3 = **2**
9 PAr_3 = **3**

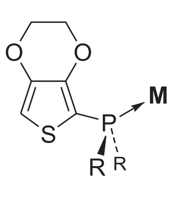
The product identities were confirmed through a combination of IR, NMR, and mass spectroscopies. The ^{31}P NMR chemical shifts (see Table 2) of the complexes are 52–60 ppm upfield relative to the chemical shifts of the free ligand, indicative of P-coordinated phosphines. The proton and carbon NMR suggest simple P-monodentate coordination modes for all three phosphines; no evidence of either cyclometallation of S-donating binding is detected. The ^{13}C

NMR spectra were particularly informative as the magnitude of the carbon–phosphorus coupling constants to the carbonyl groups provided strong support for the cis-disubstituted geometry of **7** as well as the monosubstituted nature of **8** and **9**. Parent molecular anions were observed in the mass spectra of all three complexes. However, these are all relatively weak compared with the base peaks, which in each case correspond to the loss of two carbonyls. This process may well be facilitated by chelation of an ethylenedioxy oxygen atom of the EDOT–phosphines (see the following). The ν(CO) frequencies are quite similar to those observed in related molybdenum carbonyl complexes of 2-thienylphosphines, a feature that suggests that the π-electron-rich nature of the EDOT moiety is not strongly felt by the metal center in these complexes.

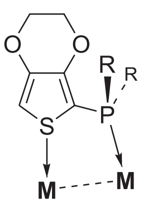
Cyclic voltammetry studies on complexes **7**–**9** revealed irreversible oxidations for all three compounds. Interestingly, the oxidation peak potential for complexes **8** and **9** are very similar to the peak potentials for the corresponding free ligand, whereas the peak potential for **7** is some 0.4 V lower than its free phosphine ligand. This may be related to the fact that **7** has two EDOT phosphine ligands whereas **8** and **9** have one each, although the irreversibility of the oxidations renders direct comparisons difficult owing to the scan rate dependence of these processes. Attempts to electropolymerize **7**–**9** by repeated electrochemical cycling failed, instead leading to electrode passivation.

Conclusions

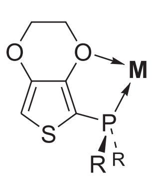
We have described the synthesis and characterization of a new series of phosphines bearing ethylenedioxythiophene substituents. Characterization of the phosphines as well as metal complexes thereof suggest there is little electronic perturbation of the EDOT group by the phosphine and vice versa. In sharp contrast to other lone-pair-containing substituents (e.g., -OR, -SR) that can enhance the redox stability of thiophenes, phosphine groups do not offer much in the way of electrochemical stability at all and in fact can destabilize the otherwise inherently robust redox characteristics of the EDOT moiety. In a similar vein, it appears that the electron richness of the EDOT ring is not manifested in a more "electron-rich" metal center in coordination complexes — at least for the ones presented herein. Nonetheless, these compounds should be useful additions to the stable of arylphosphine ligands because of their ease of synthesis, variable steric bulk, and in particular because of the potential modes of coordination they offer: As simple monodentate mode **A**, bidentate (P/S) bridging ligands in polynuclear systems **B**, or chelating (P/O) chelating **C** — the latter two having the potential to be hemilabile coordination modes (16). Studies aimed at exploring the potential coordinative versatility of these ligands are in progress.



A



B



C

Experimental

General considerations

All reagents were purchased from Aldrich and used as received; $Mo(CO)_4(piperdine)_2$ was prepared according to literature procedures (15). All reactions were performed under an atmosphere of dry argon using standard Schlenk or glove box techniques. Solvents were dried and distilled under argon prior to use (CH_2Cl_2, CaH_2; THF, Na–benzophenone). Mass spectra were recorded on a Kratos Concept IH mass spectrometer system. IR spectra were recorded as Nujol mulls or KBr presses on a PerkinElmer Spectrum One spectrometer. NMR spectra were recorded on a Bruker AMX360 spectrometer. Cyclic voltammetry experiments were performed using a CV-50W voltammetric analyzer (BAS) at room temperature (22 ± 2 °C). Voltammetric measurements were performed in CH_2Cl_2 containing 1 mol/L of n-Bu_4NBF_4. The platinum electrode (BAS, diameter 1.6 mm) was used as the working electrode. Platinum and silver wires were used as auxiliary and reference electrodes, respectively. The reference electrode was calibrated vs. ferrocene/ferrocenium redox ($E°$ = 0.440 vs. Ag/AgCl) internal reference. The working electrode was polished on alumina before use. *iR* compensations were applied for all experiments.

General synthesis of (3,4-ethylenedioxy-2-thienyl) phosphine derivatives

The synthesis of EDOT-substituted phosphines **1**–**4** is exemplified by the synthesis of **1**. EDOT (1.313 g, 9.25 mmol) was dissolved in THF (50 mL) and treated with *n*-BuLi (1.6 mol/L, 3 mL, 9.36 mmol) at room temperature. After 2 h of stirring, the mixture was cooled to –78 °C and chlorodiphenylphosphine (3 mL, 3.1 mmol) was added dropwise to the reaction mixture. The mixture was stirred at –78 °C for 2 h and gradually brought to room temperature. The mixture was then poured into water (100 mL) and extracted using CH_2Cl_2 (2 × 100 mL). The organic layers were combined and dried over anhydr. $MgSO_4$. Removal of the solvent gave a crude product, which was purified by chromatography using silica gel and chloroform as the eluent. The product was then recrystallized in CH_2Cl_2–methanol.

(3,4-Ethylenedioxy-2-thienyl)diphenylphosphine (EDOT-PPh_2, 1)

Yield: 74%; mp 84 °C. UV–vis (CH_2Cl_2): λ_{max} (ε) 274 nm (16 450 M^{-1} cm^{-1}). ^1H NMR (CD_2Cl_2, 300 MHz) δ: 4.20 (m, 4H), 6.60 (s, 1H), 7.40 (m, 10H). ^{13}C NMR (CD_2Cl_2, 125 MHz) δ: 64.94 (CH_2), 65.41 (CH_2), 106.22 (CH), 109.95 (C, d, J = 28.6 Hz), 128.75 (4CH, d, J = 6.8 Hz), 129.23 (2CH), 133.54 (4CH, d, J = 20.2 Hz), 137.24 (2C, d, J = 8.6 Hz), 142.72 (C, d, J = 3.7 Hz), 147.01 (2C, d, J = 18.9 Hz). ^{31}P NMR (CD_2Cl_2, 145 MHz) δ: –28.12. HR-MS calcd. for $C_{18}H_{15}O_2PS$: 326.0530; found: 326.0535. Anal. calcd. for $C_{18}H_{15}O_2P$ (%): C 66.25, H 4.63, O 9.80; found: C 66.21, H 4.17, O 9.95.

Bis(3,4-ethylenedioxy-2-thienyl)phenylphosphine ((EDOT)$_2$PPh, 2)

Yield: 74%; mp 137 °C. UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) 274 nm (21 500 M^{-1} cm^{-1}). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 4.20 (m, 8H), 6.60 (s, 2H), 7.40 (m, 5H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ: 64.91 (2CH$_2$), 65.42 (2CH$_2$), 106.31 (2CH), 109.22 (C, d, J = 25.5 Hz), 128.62 (2CH, d, J = 6.8 Hz), 129.12 (CH), 132.48 (2CH, d, J = 19.8 Hz), 136.95 (2C, d, J = 6.3 Hz) 142.53 (2C, d, J = 4 Hz), 146.90 (2 C, d, J = 20.5 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 145 MHz) δ: –50.5. HR-MS calcd. for $C_{18}H_{15}O_4PS_2$: 390.0149; found: 390.0144. Anal. calcd. for $C_{18}H_{15}O_4PS_2$ (%): C 55.38, H 3.87, O 16.39; found: C 54.60, H 3.89, O 16.39.

Tris(3,4-ethylenedioxy-2-thienyl)phosphine ((EDOT)$_3$P, 3)

Yield: 77%; mp 181 °C. UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) 277 nm (25 450 M^{-1} cm^{-1}). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 4.20 (m, 12H), 6.60 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ: 64.90 (CH$_2$), 65.43 (CH$_2$), 106.15 (CH), 108.75 (C, d, J = 22.6 Hz), 142.47 (C, d, J = 4.5 Hz), 146.14 (C, d, J = 21.5 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 145 MHz) δ: –50.54. HR-MS calcd. for $C_{18}H_{15}O_6PS_3$: 453.9768; found: 453.9757. Anal. calcd. for $C_{18}H_{15}O_6PS_3$ (%): C 47.57, H 3.33, O 21.12; found: C 47.07, H 3.17, O 21.97.

2,5-Bis(diphenylphosphinyl)-3,4-ethylenedioxythiophene (Ph$_2$P-EDOT-PPh$_2$, 4)

Yield: 63%; mp 101 °C. UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) 292 nm (25 230 M^{-1} cm^{-1}). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 4.20 (s, 4H), 7.40 (m, 20H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ: 65.14 (CH$_2$), 116.35 (C, d, J = 31.3 Hz), 128.74 (CH, d, J = 7.5 Hz), 129.29 (CH), 133.57 (CH, d, J = 20.4 Hz), 136.79 (C, d, J = 8.8 Hz), 146.91 (C, dd, J = 2.9 Hz, J = 17.9 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 145 MHz) δ: –26.5. HR-MS calcd. for $C_{30}H_{24}O_2P_2S$: 510.0972; found: 510.0963. Anal. calcd. for $C_{30}H_{24}O_2P_2S$ (%): C 70.58, H 4.74, O 6.27, P 12.13; found: C 67.97, H 4.48, O 6.67, P 11.67.

2-Diphenylphosphinyl-5-mesitylthio-3,4-ethylenedioxythiophene (MesS-EDOT-PPh$_2$, 5)

Yield: 70%; mp 102 °C. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 2.30 (s, 3H), 2.50 (s, 6H), 4.2 (m, 4H), 6.90 (s, 2H), 7.30 (m, 10H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ: 21.33 (CH$_3$), 22.34 (2CH$_3$), 65.35 (CH$_2$), 65.37 (CH$_2$), 110.97 (2C, d, J = 31.6 Hz), 116.00 (2C), 128.97 (4CH, d, J = 6.8 Hz), 129.48 (2CH), 129.79 (2CH) 133.68 (4CH, d, J = 19.2 Hz), 137.12 (C, d, J = 7.9), 139.65 (C), 142.65 (C, d, J = 3.4 Hz), 143.21 (C), 146.71 (2C, d, J = 19.2 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 145 MHz) δ: –27.6. HR-MS calcd. for $C_{27}H_{25}O_6PS_2$: 476.1034; found: 476.1033. Anal. calcd. for $C_{27}H_{25}O_6PS_2$ (%): C 68.04, H 5.29, O 6.71, P 7.93; found: C 67.58, H 4.96, O 7.12, P 6.08.

Syntheses of **cis**-*Mo(CO)$_4$*(**PAr$_3$**)$_2$ *(7,* **PAr$_3$ =** *1)*

A solution of **1** (0.652 g, 2 mmol) in CH$_2$Cl$_2$ (2 mL) was added dropwise to a stirred slurry of *cis*-Mo(CO)$_4$(piperidine)$_2$ (0.380 g, 1 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The mixture was stirred overnight and filtered through a pad of silica gel. After filtration, the solution was concentrated and the product was precipitated by the addition of pentane. The complex was isolated as a white solid (yield 43%); mp 115 °C. IR ν(CO) cm^{-1}: 2023, 1924, 1908, 1878. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 4.10 (m, 8H), 6.60 (d, J = 2.10 Hz, 2H), 7.20 (m, 8H), 7.40 (m, 12). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ: 64.60 (CH$_2$), 64.80 (CH$_2$), 105.50 (CH), 109.80 (C, dd, J = 12.5 Hz), 128.30 (C, t, J = 4.6 Hz), 130.00 (CH) 133.40 (C, t, J = 6.8 Hz), 135.90 (C, dt, J = 15.5 Hz), 143.20 (C, t, J = 3 Hz), 145.70 (C, t, J = 3.7 Hz), 210.20 (C, t, J = 9.4 Hz), 215.6 (C, t, J = 9.3 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 145 MHz) δ: 24.3. HR-MS calcd. for $C_{40}H_{30}MoO_8P_2S_2$: 861.9912; found: 861.9911. Anal. calcd. for $C_{40}H_{30}MoO_8P_2S_2$ (%): C 55.82, H 3.51, O 14.87, P 7.20; found: C 54.70, H 3.67, O 15.36, P 7.07.

Syntheses of Mo(CO)$_5$(**PAr$_3$**) *(8,* **PAr$_3$ =** *2)*

Complex **8** was prepared in an analogous fashion to **9**. Yield: 70%; mp 172 °C. Irν(CO) cm^{-1}: 1946. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 4.20 (s, 8H) 6.70 (d, J = 2.2 Hz, 2H), 7.40 (m, 3H), 7.60 (m, 3H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ: 64.90 (CH$_2$), 65.30 (CH$_2$),106.70 (CH, d, J = 2.4 Hz), 128.8 (CH, d, J = 9.8 Hz), 130.8 (CH), 132.20 (CH, d, J = 13.1 Hz), 135.30 (C, d, J = 39.9 Hz), 143.20 (C, d, J = 6.4 Hz), 146.4 (C, d, J = 8.1 Hz), 206.40 (C, d, J = 9.5 Hz), 211.60 (C, d, J = 24.7 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 145 MHz) δ: 7.6. HR-MS calcd. for $C_{23}H_{15}MoO_9PS_2$: 627.8950; found: 627.8985.

Syntheses of Mo(CO)$_5$(**PAr$_3$**) *(9,* **PAr$_3$ =** *3)*

cis-Mo(CO)$_4$(piperidine)$_2$ (1.154 g, 3 mmol) was added to a solution of **3** (0.422 g, 0.9 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The mixture was stirred overnight and filtered through a pad of silica gel. The product was isolated by precipitation from pentane. Yield: 60%; mp 202 °C. IR ν(CO) cm^{-1}: 1947. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 4.10 (m, 8H), 6.60 (d, J = 2.9 Hz, 2H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz) δ: 64.70 (CH$_2$), 65.00 (CH$_2$), 106.30 (CH), 107.10 (C, d, J = 36.7 Hz), 142.70 (C, d, J = 7.3 Hz), 145.8 (C, d, J = 10.6 Hz), 206.0 (C, d, J = 9.5 Hz), 211.60 (C, d, J = 24.6 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 145 MHz) δ: –8.5. HR-MS calcd. for $C_{23}H_{15}MoO_{11}PS_3$: 691.8569; found: 691.8618. Anal. calcd. for $C_{23}H_{15}MoO_{11}PS_3$ (%): C 40.01, H 2.19, O 25.49, S 13.93, P 4.49; found: C 39.99, H 2.22, O 25.65, S 14.34, P 4.44.

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