

Spring 4-13-2017

Design, Synthesis, and Characterization of a Phosphine-based Heterotrimetallic (M = Fe, Ru, W) Homopolymer

Joe Gilroy
jgilroy5@uwo.ca

Amir Rabiee Kenaree

Follow this and additional works at: <https://ir.lib.uwo.ca/chempub>

 Part of the [Chemistry Commons](#)

Citation of this paper:

Gilroy, Joe and Rabiee Kenaree, Amir, "Design, Synthesis, and Characterization of a Phosphine-based Heterotrimetallic (M = Fe, Ru, W) Homopolymer" (2017). *Chemistry Publications*. 77.
<https://ir.lib.uwo.ca/chempub/77>

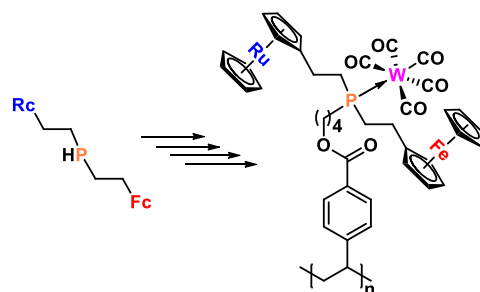
Design, Synthesis, and Characterization of a Phosphine-based Heterotrimetallic (M = Fe, Ru, W) Homopolymer

Amir Rabiee Kenaree and Joe B. Gilroy*

Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research (CAMBR), The University of Western Ontario, London, Ontario, Canada, N6A 5B7.

Supporting Information Placeholder

ABSTRACT: An organometallic homopolymer containing three different metals per repeating unit was synthesized from an air- and moisture-stable secondary phosphine bearing ethylferrocene and ethylruthenocene groups. Hydrophosphination yielded a tertiary phosphine bearing an alcohol, which was then used to introduce a polymerizable styrene group via DCC coupling. Free-radical polymerization, followed by post-polymerization coordination to photo-generated $W(CO)_5$ units yielded the title polymer, which showed thermal, spectroscopic, and electrochemical properties associated with each of the transition metals involved.

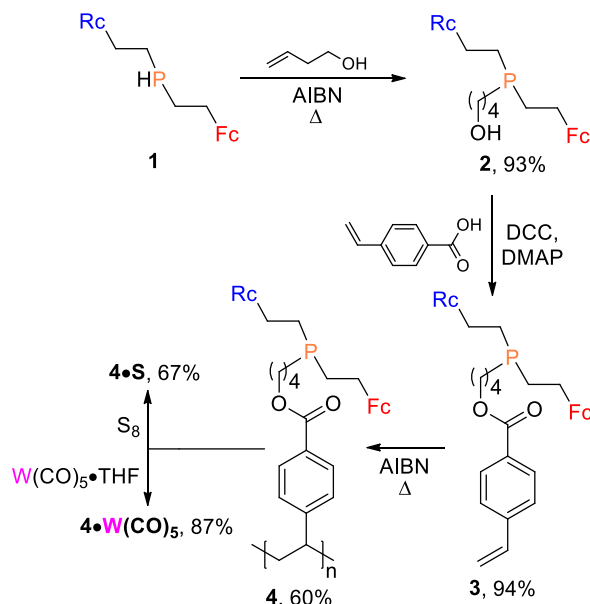


Metallopolymers have long received interest due to the combination of traits they possess, including the thermal/solution processability traditionally associated with polymers and the functionality (*e.g.*, redox activity, magnetism, catalysis) associated with transition metals.¹⁻⁴ The complexity of metallopolymer structures has increased as the field has evolved, and metallopolymers bearing multiple transition metals per repeating unit are now being targeted. Several strategies for the production of heterobimetallic polymers exist, including: post-polymerization functionalization,⁵⁻⁷ polymerization of heterobimetallic monomers,^{6,8-10} and copolymerization of monomers containing different metals.¹¹⁻¹⁴

While advances in synthetic protocols have been widespread, heterotrimetallic polymers that take advantage of the properties of three different metals remain scarce.¹⁵⁻¹⁶ In this brief communication, we report the synthesis, characterization, and electrochemistry of a rare example of a metallopolymer bearing three different transition metals per repeating unit. In doing so, we have also expanded the subclass of phosphorus-based metallopolymers.¹⁷⁻²²

The synthetic strategy employed in this study is outlined in Scheme 1. The radical-catalyzed hydrophosphination of 3-buten-1-ol starting from secondary phosphine **1**,²³ which bears ethylruthenocene and ethylferrocene substituents, resulted in the formation of tertiary phosphine **2** in 93% yield. DCC coupling (DCC = *N,N'*-dicyclohexylcarbodiimide) in the presence of dimethylaminopyridine (DMAP) yielded monomer **3** in 94% yield. These molecular species were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy, FT-IR and UV-Vis absorption spectroscopy, mass spectrometry and elemental analysis (Table S1, Figures S1–S8). The free-radical polymerization of phosphines and related sulfides/oxides dates back to the 1960s.²⁴ In this case, free-radical polymerization of monomer

3 resulted in the formation of heterobimetallic polymer **4** (60%), with a polystyrene backbone. The pendant phosphine moieties in polymer **4** were coordinated to $W(CO)_5$ units, which were generated via photolysis of $W(CO)_6$ in THF, to yield heterotrimetallic polymer **4•W(CO)₅** in 87% yield. The polymers described are soluble in halogenated CH_2Cl_2 and $CHCl_3$ and sparingly soluble in THF. They were characterized by ¹H and ³¹P NMR spectroscopy, FT-IR and UV-Vis absorption spectroscopy, and gel permeation chromatography (GPC) (Tables S1 and S2, Figures 1 and S9–S12).



Scheme 1. Synthesis of heterometallic polymers **4**, **4•S**, and **4•W(CO)₅**. Rc = ruthenocene, Fc = ferrocene.

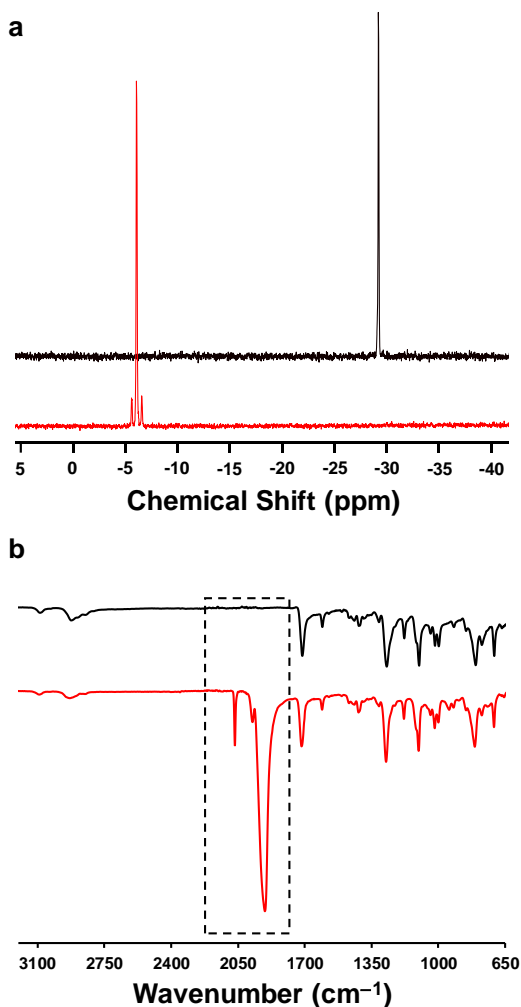


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (a) and FT-IR spectra (b) for polymers **4** (black lines) and **4**·**W(CO)₅** (red lines). The dashed box highlights the region of the IR spectra associated with carbonyl stretching frequencies.

The free-radical polymerization of monomer **3** was accompanied by the disappearance of the ^1H NMR signals associated with the mono-substituted alkene [6.76 ppm (d of d), 5.87 ppm (d), and 5.39 ppm (d)] group and the appearance of broad signals (1–2 ppm) associated with the saturated polystyrene backbone of polymer **4**. Upon coordination of each of the phosphine groups present in polymer **4** to **W(CO)₅**, the singlet observed in the ^{31}P NMR spectrum of polymer **4** (δ : -29.2 ppm) disappeared. Polymer **4**·**W(CO)₅** gave rise to a new ^{31}P NMR signal (δ : -6.1 ppm) upfield of that of the free phosphine polymer. The shifted signal was accompanied by satellites associated with ^{31}P - ^{183}W coupling ($^1J_{\text{PW}} = 233$ Hz), confirming that each pendant phosphine group had been coordinated to tungsten (Figure 1a). FT-IR spectroscopy was also used to monitor the post-polymerization coordination chemistry. As demonstrated in Figure 1b, three different CO stretches [$\nu(\text{CO})$: 1909, 1974, and 2066 cm^{-1}] were observed in the spectrum of **4**·**W(CO)₅**, which was otherwise very similar to that of polymer **4**. These data are consistent with those of closely related molecular species,²⁵ and support our previous conclusion that the pendant phosphine groups have been quantitatively converted to the corresponding $\text{R}_3\text{P} \rightarrow \text{W}(\text{CO})_5$ complexes (Figure 1b).

GPC analysis of polymers **4** and **4**·**W(CO)₅** proved challenging. The polymers are poorly soluble in common GPC solvents, including H_2O and DMF, and had limited solubility in THF. Furthermore, the direct analysis of polymer **4** was not possible due to significant polymer-column interactions, requiring conversion to **4**·**S** through oxidation with elemental sulfur. The GPC data collected for the soluble portions **4**·**S** and **4**·**W(CO)₅** in THF represent minimum estimates of their molecular weight, and confirm their high polymer character (Table S2, Figure S13, **4**·**S**: $M_n = 9,700$ g mol^{-1} , $D = 1.46$; **4**·**W(CO)₅**: $M_n = 11,600$ g mol^{-1} , $D = 2.41$). It must be noted that the GPC trace collected for **4**·**W(CO)₅** also contained evidence of aggregate formation, potentially caused by intermolecular reactions involving the relatively polar carbonyl groups. Prolonged stirring in warm THF, even in dilute solution, did not result in the removal of the aggregate species in solution.

The differential scanning calorimetry (DSC) data collected for **4** and **4**·**W(CO)₅** are consistent with the hypothesis that the **W(CO)₅** groups enhance intermolecular interactions. This behavior is manifested as an increase in glass transition temperature (T_g) from 52 $^\circ\text{C}$ for **4** to 92 $^\circ\text{C}$ for **4**·**W(CO)₅** (Figure S14). Thermal gravimetric analysis (TGA) also revealed marked differences for polymers **4** and **4**·**W(CO)₅**. The onset of decomposition was *ca.* 220 $^\circ\text{C}$ for both polymers, and significantly, the char yields at 1000 $^\circ\text{C}$ of 24.0% (**4**) and 32.1% [**4**·**W(CO)₅**] were consistent with the metal content for the respective polymers (22.2% and 32.0%) (Figure S15).

The UV-Vis absorption spectra for each of the molecular and polymeric species described contain features associated with formally forbidden $d \rightarrow d$ transitions arising from ferrocene (*ca.* 440 nm) and ruthenocene (*ca.* 320 nm) that were consistent with those observed for related phosphines and metal complexes (Figure S16).^{23,25}

The electrochemical properties of compounds **1–3** and polymers **4** and **4**·**W(CO)₅** were explored using cyclic voltammetry (Table S1, Figures 2, S17–S18). The supporting electrolyte chosen for these studies was $[\textit{n}\text{-Bu}_4\text{N}][\text{OTf}]$, as the triflate anion enhances the solubility of the electrogenerated polycations implicated in these studies. The voltammogram recorded for **4** was comprised of several distinct features, including: an irreversible wave at -150 mV (relative to the ferrocene/ferrocenium redox couple) associated with the oxidation of ferrocene in species adsorbed to the working electrode surface,^{23,26–27} a ferrocene oxidation wave with reversible character at -15 mV, and an irreversible oxidation associated with ruthenocene at 400 mV. The current response of the wave centered at -150 mV was less than that expected for a one electron process, ruling out the possibility that it results from phosphine oxidation. Furthermore, the adsorption behavior observed has been previously explored in detail for closely related phosphines.^{21,23–24} The electrochemical properties of ruthenocene are far more complex than those of ferrocene, due to the extremely Lewis acidic character of ruthenocenium that often leads to the formation of acid/base adducts and/or disproportionation and dimerization reactions.^{23,28–29} This behavior is responsible for the irreversible character of the ruthenocene oxidation wave, and also effects the shape and symmetry of the ferrocene wave mentioned above. Upon coordination to tungsten, the electrochemical properties of **4**·**W(CO)₅** changed dramatically, revealing independent electrochemical features associated with each of the transition metals present. Firstly, as has been observed for related

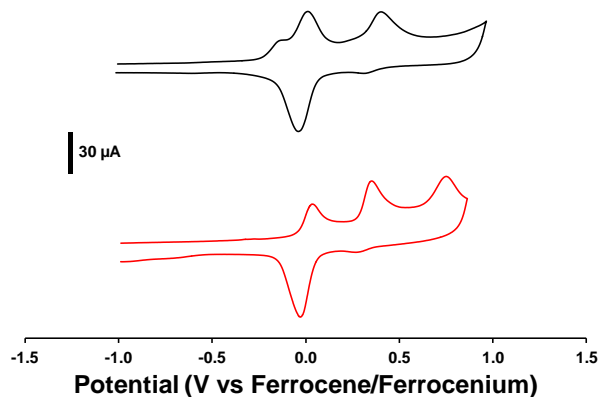


Figure 2. Cyclic voltammograms of polymers **4** (black line) and **4•W(CO)₅** (red line) recorded at 250 mV s⁻¹ in solutions of 1 mM solutions in THF containing 0.1 M [*n*-Bu₄N][OTf] as supporting electrolyte.

molecular species,²⁵ the irreversible wave associated with phosphine adsorption at the working electrode disappeared. The ferrocene oxidation (0 mV) became less symmetric and was shifted slightly to more positive potentials. The irreversible oxidation of the ruthenocene moieties, observed at a potential of 350 mV, was once again observed for **4•W(CO)₅** and was essentially unchanged. Finally, an irreversible wave corresponding to the oxidation of tungsten was observed at a potential of 750 mV. This behavior was consistent with that observed for related halopentacarbonyltungsten complexes.³⁰⁻³¹

In this work, we have described the synthesis and characterization of polymers bearing two and three different metals per repeating unit. The polymers display thermal, spectroscopic, and electrochemical properties associated with each transition metal. We feel that the synthetic strategy described has the potential to open up a new area of metalopolymer chemistry, and our future work in this area will focus on expanding the scope of the chemistry of heterotrimetallic polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, NMR and UV-Vis absorption spectra, DSC, TGA, and GPC data, and additional CVs (PDF).

AUTHOR INFORMATION

Corresponding Author

* J.B.G.: E-mail, joe.gilroy@uwo.ca; Tel, +1-519-661-2111 ext 81561.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the University of Western Ontario, NSERC of Canada (DG, 435675), the Ontario Ministry of Research and Innovation (ERA, ER14-10-147) and the Canada Foundation for Innovation (JELF, 33977) for funding this work. We also thank Prof. Paul J. Ragona for helpful discussions and access to instrumentation in his laboratory.

REFERENCES

- (1) Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I. *Nat. Mater.* **2011**, *10*, 176–188.
- (2) Hardy, C. G.; Zhang, J.; Yan, Y.; Ren, L.; Tang, C. *Prog. Polym. Sci.* **2014**, *39*, 1742–1796.
- (3) Hailes, R. L. N.; Oliver, A. M.; Gwyther, J.; Whittell, G. R.; Manners, I. *Chem. Soc. Rev.* **2016**, *45*, 5358–5407.
- (4) Pietschnig, R. *Chem. Soc. Rev.* **2016**, *45*, 5216–5231.
- (5) Chan, W. Y.; Clendenning, S. B.; Berenbaum, A.; Lough, A. J.; Aouba, S.; Ruda, H. E.; Manners, I. *J. Am. Chem. Soc.* **2005**, *127*, 1765–1772.
- (6) Zamora, M.; Bruña, S.; Alonso, B.; Cuadrado, I. *Macromolecules* **2011**, *44*, 7994–8007.
- (7) Paquette, J. A.; Gilroy, J. B. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 3257–3266.
- (8) Dong, Q.; Li, G.; Ho, C.-L.; Faisal, M.; Leung, C.-W.; Pong, P. W.-T.; Liu, K.; Tang, B.-Z.; Manners, I.; Wong, W.-Y. *Adv. Mater.* **2012**, *24*, 1034–1040.
- (9) Erhard, M.; Lam, K.; Haddow, M.; Whittell, G. R.; Geiger, W. E.; Manners, I. *Polym. Chem.* **2014**, *5*, 1264–1274.
- (10) Rabiee Kenaree, A.; Gilroy, J. B. *Dalton Trans.* **2016**, *45*, 18229–18240.
- (11) Gilroy, J. B.; Patra, S. K.; Mitchels, J. M.; Winnik, M. A.; Manners, I. *Angew. Chem. Int. Ed.* **2011**, *50*, 5851–5855.
- (12) Zha, Y.; Thaker, H. D.; Maddikeri, R. R.; Gido, S. P.; Tuominen, M. T.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 14534–14541.
- (13) Zhang, J.; Yan, Y.; Chen, J.; Chance, W. M.; Hayat, J.; Gai, Z.; Tang, C. *Chem. Mater.* **2014**, *26*, 3185–3190.
- (14) Gu, H.; Ciganda, R.; Castel, P.; Ruiz, J.; Astruc, D. *Macromolecules* **2016**, *49*, 4763–4773.
- (15) Alexandru, M.-G.; Visinescu, D.; Andruh, M.; Marino, N.; Armentano, D.; Cano, J.; Lloret, F.; Julve, M. *Chem. Eur. J.* **2015**, *21*, 5429–5446.
- (16) Kuwamura, N.; Kurioka, Y.; Konno, T. *Chem. Commun.* **2017**, *53*, 846–849.
- (17) Alcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596–9603.
- (18) Noonan, K. J. T.; Gillon, B. H.; Cappello, V.; Gates, D. P. *J. Am. Chem. Soc.* **2008**, *130*, 12876–12877.
- (19) Patra, S. K.; Whittell, G. R.; Nagiah, S.; Ho, C.-L.; Wong, W.-Y.; Manners, I. *Chem. Eur. J.* **2010**, *16*, 3240–3250.
- (20) Wang, X.; Cao, K.; Liu, Y.; Tsang, B.; Liew, S. *J. Am. Chem. Soc.* **2013**, *135*, 3399–3402.
- (21) Pandey, S.; Loennecke, P.; Hey-Hawkins, E. *Eur. J. Inorg. Chem.* **2014**, *2014*, 2456–2465.
- (22) Rabiee Kenaree, A.; Berven, B. M.; Ragona, P. J.; Gilroy, J. B. *Chem. Commun.* **2014**, *50*, 10714–10717.
- (23) Rabiee Kenaree, A.; Cuthbert, T. J.; Barbon, S. M.; Boyle, P. D.; Gillies, E. R.; Ragona, P. J.; Gilroy, J. B. *Organometallics* **2015**, *34*, 4272–4280.
- (24) Rarikowitz, R.; Marcus, R.; Pellon, J. *J. Polym. Sci., Part A: Polym. Chem.* **1964**, *2*, 1241–1249.
- (25) Rabiee Kenaree, A.; Sauve, E. R.; Ragona, P. J.; Gilroy, J. B. *Dalton Trans.* **2016**, *45*, 2859–2867.
- (26) Downard, A. J.; Goodwin, N. J.; Henderson, W. *J. Organomet. Chem.* **2003**, *676*, 62–72.
- (27) Seibert, A. R.; Cain, M. F.; Glueck, D. S.; Nataro, C. *J. Organomet. Chem.* **2011**, *696*, 2259–2262.
- (28) Swarts, J. C.; Nafady, A.; Roudebush, J. H.; Trupia, S.; Geiger, W. E. *Inorg. Chem.* **2009**, *48*, 2156–2165.
- (29) Russell, A. D.; Gilroy, J. B.; Lam, K.; Haddow, M. F.; Harvey, J. N.; Geiger, W. E.; Manners, I. *Chem. Eur. J.* **2014**, *20*, 16216–16227.
- (30) Bond, A. M.; Bowden, J. A.; Colton, R. *Inorg. Chem.* **1974**, *13*, 602–608.
- (31) Abbott, A. P.; Malkov, A. V.; Zimmermann, N.; Raynor, J. B.; Ahmed, G.; Steele, J.; Kočovský, P. *Organometallics* **1997**, *16*, 3690–3695.