Heterotrimetallic M−M′−M″ Transition Metal Complexes Based on 1,3,5-Triethynylbenzene: Synthesis, Solid State Structure, and Electrochemical and UV−Vis Characterization. EPR Analysis of the *in Situ* Generated Associated Radical Cations

Rico Packheiser,[§] Petra Ecorchard,[§] Tobias Rüffer,[§] Manja Lohan,[§] Björn Bräuer,[§]
Frédéric Justaud,[§] Claude Lapinte,*,[†] and Heinrich Lang*,[†]

Lehrstuhl für Anorganische Chemie, Institut für Chemie, Fakultät für Naturwissenschaften, Technische Universität Chemnitz, Strasse der Nationen 62, 09111 Chemnitz, Germany, and Sciences Chimiques de Rennes, Université de Rennes-1−CNRS (UMR 6226), Campus de Beaulieu, 35042 Rennes Cedex, France

The synthesis of a series of complexes with different organometallic building blocks unsymmetrically arranged around the periphery of a 1,3,5-triethynylbenzene core is discussed. They are accessible by diverse consecutive reaction sequences, which allow the introduction of transition metal units such as Fc, [(^{t}Bu$_2$bpy)(CO)$_3$Re], [(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$Ru], [(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$Os], and *trans*-[(Ph$_3$P)$_2$(Cl)Pt] (Fc = (η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)Fe; ^{t}Bu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl). The solid state structures of five complexes have been determined. The electrochemical behavior of the newly synthesized mono-, heterobi-, and heterotrimetallic assemblies have been studied, showing that there is no significant electronic interaction between the respective metal atoms. UV−vis spectroscopic measurements suggest a weak interaction between the appropriate metal atoms. The associated radical cations were *in situ* generated by stepwise chemical oxidation and characterized by continuous wave electron paramagnetic resonance (EPR) investigations in X-band performed at low temperatures.

Introduction

The chemistry of carbon-rich, π-conjugated, and rigid-structured organometallic molecules is of fundamental interest and has captured much attention, due to the manifold attractive properties associated with some of these compounds.[1] In recent years many homo- and heterobimetallic complexes with organic and/or inorganic connecting units have been designed and synthesized, and their chemical and physical properties were intensively studied.[1] However, less is known about transition metal complexes in which more than two different metal atoms are linked through a common bridging ligand. So far, unsatur-ated carbon ligands such as alkynyls,[2,3] (poly)phenyleneethynyl-enes,[4–6] arylethenyls,[7] or cumulenes[8] were used as connecting units to span diverse metal atoms. One example is 1,3,5-triethynylbenzene, which can act as a core in organometallic chemistry to prepare symmetrical and unsymmetrical transition metal complexes.[9,10] Due to its geometry and active coordination sites, this molecule allows extension of the core in three directions by using, for example, dehydrohalogenation or C−C coupling reactions. Symmetric homosubstitution around the benzene core by iron-, iridium-, chromium-, gold-, and platinum-containing metal building blocks has been achieved,[9] and heterometallic complexes of triethynylbenzene featuring, for example, *trans*-[(dppm)$_2$(Cl)Ru], *trans*-[(dppm)$_2$(Cl)Os], [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru] (dppm = bis(diphenylphosphino)methane),

* To whom correspondence should be addressed. E-mail: heinrich.lang@chemie.tu-chemnitz.de (H.L.); claude.lapinte@univ-rennes1.fr (C.L.).
§ Technische Universität Chemnitz.
† Université de Rennes-1–CNRS.
(1) For example:(a) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003,** 42, 2586. (b) Yam, V. W. W.; Lo, K. K. W.; Wong, K. M. C. *J. Organomet. Chem.* **1999,** 578, 3. (c) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996,** 96, 759. (d) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998,** 31, 26. (e) Powell, C. E.; Humphrey, M. G. *Coord. Chem. Rev.* **2004,** 248, 725. (f) Cifuentes, M. P.; Humphrey, M. G.; Morall, J. P.; Samoc, M.; Paul, F.; Roisnel, T.; Lapinte, C. *Organometallics* **2005,** 24, 4280. (g) Low, P. J. *Dalton Trans.* **2005,** 17, 2821. (h) Long, N. J.; Angela, A. J.; de Biani, F. F.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1998,** 2017. (i) Köllner, C.; Pugin, B.; Togni, A. *J. Am. Chem. Soc.* **1998,** 120, 10274. (j) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996,** 118, 9635. (k) Hu, Q. S.; Pugh, V.; Sabat, M.; Pu, L. *J. Org. Chem.* **1999,** 64, 7528. (l) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998,** 178, 180–431. (m) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002,** 31, 168. (n) Nelson, S. F. In *Electron Transfer in Chemistry;* Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 1,Chapter 10. (o) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000,** 33, 755. (p) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. *Coord. Chem. Rev.* **2004,** 248, 683. (q) Ward, M. D. *Chem. Soc. Rev.* **1995,** 121. (r) Astruc, D. *Acc. Chem. Res.* **1997,** 30, 383. (s) Cifuentes, M. P.; Humphrey, M. G. *J. Organomet. Chem.* **2004,** 689, 3968.

(2) Homobimetallic systems with all-carbon bridges:(a) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004,** 50, 179. (b) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2006,** 106, PR1–PR33. (c) Bruce, M. I.; Jevric, M.; Skelton, B. W.; Smith, M. E.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **2006,** 691, 361. (d) Maurer, J.; Winter, R. F.; Sarkar, B.; Zalis, S. *J. Solid State Electrochem.* **2005,** 9, 738. (e) Coat, F.; Paul, F.; Lapinte, C.; Toupet, L.; Costuas, K.; Halet, J.-F. *J. Organomet. Chem.* **2003,** 683, 368. (f) Meyer, W. E.; Amoroso, A. J.; Horn, C. R.; Jaeger, M.; Gladysz, J. A. *Organometallics* **2001,** 20, 1115. (g) Dembinski, R.; Bartik, T.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000,** 122, 810.

(3) Heterobimetallic systems with all-carbon bridges:(a) Bruce, M. I.; Costuas, K.; Davin, T.; Ellis, B. G.; Halet, J. F.; Lapinte, C.; Low, P. J.; Smith, M. E.; Skelton, B. W.; Toupet, L.; White, A. H. *Organometallics* **2005,** 24, 3864. (b) Bruce, M. I.; Humphrey, P. A.; Jevric, M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2007,** 692, 2564. (c) Bruce, M. I.; Cole, M. L.; Gaudio, M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2006,** 691, 4601. (d) Bruce, M. I.; Ellis, B. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000,** 607, 137. (e) Bruce, M. I.; Hall, B. C.; Low, P. J.; Smith, M. E.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2000,** 300, 302–633. (f) Jiao, H.; Costuas, K.; Gladysz, J. A.; Halet, J.-F.; Guillemot, M.; Toupet, L.; Paul, F.; Lapinte, C. *J. Am. Chem. Soc.* **2003,** 125, 9511. (g) Paul, F.; Meyer, W. E.; Toupet, L.; Jiao, H.; Gladysz, J. A.; Lapinte, C. *J. Am. Chem. Soc.* **2000,** 122, 9405.

Scheme 1. Synthesis of 8
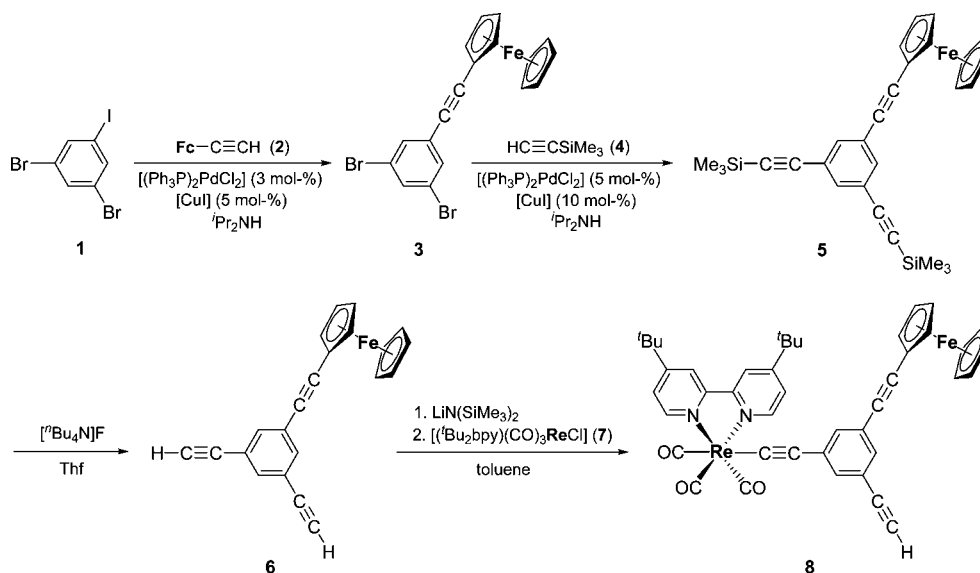
and ferrocenyl end-grafted moieties are also known.[10] Such organometallic molecules are of great interest, due to their extended π-system, which can provide reversible redox chemistry,[4a,b,5c,d,6e,9a,10c,d] luminescence properties,[1a,b,5a,b,10b] photoinduced electron or energy transfer processes,[5f,11] or even liquid crystalline behavior.[1a,12] Also applications in the field of metallo-dendrimers,[1s,9f–9j,10e,13] nonlinear optical materials,[1a,e,s,4d,h,6d,7a,9g,i,14] and molecular electronics[1r,15] are possible. However, only one example is known in which three different transition metal fragments are unsymmetrically arranged around the periphery of a 1,3,5-triethynylbenzene core.[10c]

As an extension of our previous work on the synthesis and characterization of heteromultimetallic complexes in which different early and late transition metals are connected by carbon-rich organic π-conjugated bridging units, we here describe straightforward methods for the synthesis of diverse unsymmetrical organometallic complexes based on 1,3,5-triethynyl benzene. In addition, electrochemical and UV−vis spectroscopical studies together with electron paramagnetic resonance (EPR) measurements of the corresponding radical cations prepared *in situ* by chemical oxidation were carried out.

Results and Discussion

As suitable starting material for the preparation of trinuclear σ-alkynyl complexes based on the 1,3,5-ethynylbenzene core, 1-(FcC≡C)-3,5-(HC≡C)$_2$C$_6$H$_3$ (**6**) (Fc = (η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)Fe) was selected, because alkynyl ferrocenes are known to be very robust to further reactions, are electron-rich, and show a reversible redox chemistry.[9a,16] Complex **6** is known in literature, but its synthesis and characterization has not been reported so far.[10c] For this reason, a straightforward high-yield synthesis procedure for **6** was developed (Scheme 1).

To increase the selectivity of the Sonogashira carbon−carbon cross-coupling reaction, we used 1-iodo-3,5-dibromobenzene (**1**) instead of 1,3,5-tribromobenzene.[9a] This versatile single-step reaction was performed by treatment of **1** with ethynylferrocene (**2**) in the stoichiometric ratio of 1:1 at ambient temperature (Scheme 1), whereby mononuclear 1-(FcC≡C)-3,5-Br$_2$C$_6$H$_3$ (**3**) could be isolated in 85% yield. The introduction of the alkynyl substituents in **3** was accomplished by a two-step synthesis methodology by reacting **3** with trimethylsilylacetylene (**4**) to give 1-(FcC≡C)-3,5-(Me$_3$SiC≡C)$_2$C$_6$H$_3$ (**5**), which after desilylation with [^{n}Bu$_4$N]F produced **6** (Scheme 1).

For the synthesis of heterobimetallic 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(HC≡C)C$_6$H$_3$ (**8**) (^{t}Bu$_2$bpy = 4,4′-

(4) Homometallic systems with aryldiethynyl bridges:(a) Chawdhury, N.; Long, N. J.; Mahon, M. F.; Ooi, L.; Raithby, P. R.; Rooke, S.; White, A. J. P.; Williams, D. J.; Younus, M. *J. Organomet. Chem.* **2004**, *689*, 840. (b) de Montigny, F.; Argouarch, G.; Costuas, K.; Halet, J. F.; Roisnel, T.; Toupet, L.; Lapinte, C. *Organometallics* **2005**, *24*, 4558. (c) Callejas-Gaspar, B.; Laubender, M.; Werner, H. *J. Organomet. Chem.* **2003**, *684*, 144. (d) Hurst, S. K.; Cifuentes, M. P.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Asselberghs, I.; Persoons, A. *J. Organomet. Chem.* **2002**, *642*, 259. (e) Hurst, S. K.; Ren, T. *J. Organomet. Chem.* **2002**, *660*, 1. (f) Fraysse, S.; Coudret, S.; Launay, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 5880. (g) Back, S.; Lutz, M.; Spek, A. L.; Lang, H.; van Koten, G. *J. Organomet. Chem.* **2001**, *620*, 227. (h) Weyland, T.; Ledoux, I.; Brasselet, S.; Zyss, J.; Lapinte, C. *Organometallics* **2000**, *19*, 5235. (i) Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; Younus, M.; White, A. J. P.; Williams, D. J.; Payne, N. N.; Yellowlees, L.; Beljonne, D.; Chawdhury, N.; Friend, R. H. *Organometallics* **1998**, *17*, 3034. (j) Bruce, M. I.; Hall, B. C.; Kelly, B. D.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 3719. (k) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J. *Organometallics* **1996**, *15*, 1530.
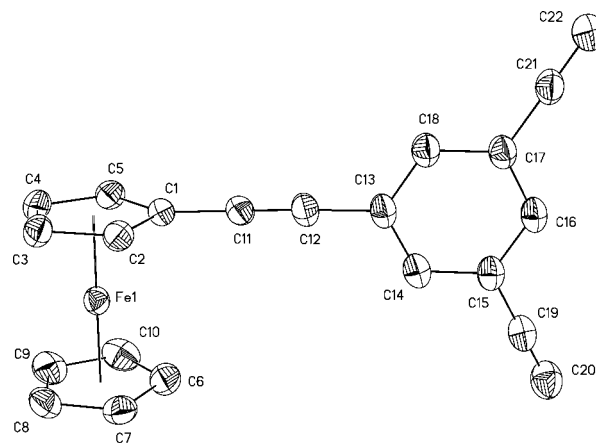(5) Heterometallic systems with aryldiethynyl bridges:(a) Lam, S. C. F.; Yam, V. W. W.; Wong, K. M. C.; Cheng, E. C. C.; Zhu, N. *Organometallics* **2005**, *24*, 4298. (b) Wong, K. M. C.; Lam, S. C. F.; Ko, C. C.; Zhu, N.; Yam, V. W. W.; Roué, S.; Lapinte, C.; Fathallah, S.; Costuas, K.; Kahlal, S.; Halet, J. F. *Inorg. Chem.* **2003**, *42*, 7086. (c) Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J. *J. Organomet. Chem.* **1998**, *570*, 55. (d) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184. (e) Samoc, M.; Gauthier, N.; Cifuentes, M. P.; Paul, F.; Lapinte, C.; Humphrey, M. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7376. (f) Monnereau, C.; Gomez, J.; Blart, E.; Odobel, F.; Wallin, S.; Fallberg, A.; Hammarström, L. *Inorg. Chem.* **2005**, *44*, 4806.
(6) Extended polyphenyleneethynyl systems:(a) Chao, H.-Y.; Lu, W.; Li, Y.; Chan, M. C. W.; Che, C.-M.; Cheung, K.-K.; Zhu, N. *J. Am. Chem. Soc.* **2002**, *124*, 14696. (b) Walters, K. A.; Ley, K. D.; Cavalaheiro, C. S. P.; Miller, S. E.; Gosztola, D.; Wasielewski, M. R.; Bussandri, A. P.; van Willigen, H.; Schanze, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8329. (c) Klein, A.; Lavastre, O.; Fiedler, J. *Organometallics* **2006**, *25*, 635. (d) Morrall, J. P.; Powell, C. E.; Stranger, R.; Cifuentes, M. P.; Humphrey, M. G.; Heath, G. A. *J. Organomet. Chem.* **2003**, *670*, 248. (e) Ghazala, S. I.; Paul, F.; Toupet, L.; Roisnel, T.; Hapiot, P.; Lapinte, C. *J. Am. Chem. Soc.* **2006**, *128*, 2463.
(7) (a) Xia, H.; Wen, T. B.; Hu, Q. Y.; Wang, X.; Chen, X.; Shek, L. Y.; Williams, I. D.; Wong, K. S.; Wong, G. K. L.; Jia, G. *Organometallics* **2005**, *24*, 562. (b) Mata, J. A.; Peris, E.; Llusar, R.; Uriel, S.; Cifuentes, M. P.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Eur. J. Inorg. Chem.* **2001**, 2113. (c) Maurer, J.; Sarkar, B.; Kaim, W.; Winter, R. F.; Záliš, S. *Chem.−Eur. J.* **2007**, *13*, 10257.
(8) Metallacumulene systems:(a) Skibar, W.; Kopacka, H.; Wurst, K.; Salzmann, C.; Ongania, K. H.; de Biani, F. F.; Zanello, P.; Bildstein, B. *Organometallics* **2004**, *23*, 1024. (b) Venkatesan, K.; Blacque, O.; Berke, H. *Organometallics* **2006**, *25*, 5190. (c) Venkatesan, K.; Fox, T.; Schmalle, H. W.; Berke, H. *Organometallics* **2005**, *24*, 2834. (d) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178−180*, 409.

di-*tert*-butyl-2,2′-bipyridyl) we used in the beginning of our studies the standard literature procedures for the preparation of [(*t*Bu₂bpy)(CO)₃Re] acetylides, i.e., the reaction of monolithiated **6** with [(*t*Bu₂bpy)(CO)₃ReCl] (**7**).[17] However, no reaction took place when diethyl ether, tetrahydrofuran, or mixtures of these solvents were used. Complex **8** was also not formed in the reaction of **6** with **7** in presence of NEt₃ and [AgOTf] (OTf = triflate, OSO₂CF₃) in refluxing tetrahydrofuran.[10b,17a,b] Thus, we developed a new synthesis method to prepare **8** by monolithiation of **6** with LiN(SiMe₃)₂ in toluene at 0 °C and refluxing the reaction mixture after addition of **7** (Scheme 1). Heterobimetallic **8** was isolated as an orange solid after column chromatography

(9) Homometallic systems with 1,3,5-triethynylbenzene:(a) Fink, H.; Long, N. J.; Martin, A. J.; Opromolla, G.; White, A. J. P.; Williams, D. J.; Zanello, P. *Organometallics* **1997**, *16*, 2646. (b) Weyland, T.; Costuas, K.; Mari, A.; Halet, J. F.; Lapinte, C. *Organometallics* **1998**, *17*, 5569. (c) Tykwinski, R. R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203. (d) Müller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 607. (e) Irwin, M. J.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Yufit, D. S. *Chem. Commun.* **1997**, 219. (f) Leininger, S.; Stang, P. J.; Huang, S. *Organometallics* **1998**, *17*, 3981. (g) Cifuentes, M. P.; Powell, C. E.; Morrall, J. P.; McDonagh, A. M.; Lucas, N. T.; Humphrey, M. G.; Samoc, M.; Houbrechts, S.; Asselberghs, I.; Clays, K.; Persoons, A.; Isoshima, T. *J. Am. Chem. Soc.* **2006**, *128*, 10819. (h) Samoc, M.; Morrall, J. P.; Dalton, G. T.; Cifuentes, M. P.; Humphrey, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 731. (i) Powell, C. E.; Morrall, J. P.; Ward, S. A.; Cifuentes, M. P.; Notaras, E. G. A.; Samoc, M.; Humphrey, M. G. *J. Am. Chem. Soc.* **2004**, *126*, 12234. (j) McDonagh, A. M.; Powell, C. E.; Morrall, J. P.; Cifuentes, M. P.; Humphrey, M. G. *Organometallics* **2003**, *22*, 1402. (k) Weyland, T.; Costuas, K.; Toupet, L.; Halet, J.-F.; Lapinte, C. *Organometallics* **2000**, *19*, 4228;(l) Antonova, A. B.; Bruce, M. I.; Humphrey, P. A.; Gaudio, M.; Nicholson, B. K.; Scoleri, N.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **2006**, *691*, 4694. (m) Albinati, A.; Leoni, P.; Marchetti, L.; Rizzato, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 5990. (n) Chin, C. S.; Kim, M.; Won, G.; Jung, H.; Lee, H. *Dalton Trans.* **2003**, 2325. (o) Lu, W.; Zhu, N.; Che, C.-M. *J. Organomet. Chem.* **2003**, *670*, 11. (p) Onitsuka, K.; Yabe, K.; Ohshiro, N.; Shimizu, A.; Okumura, R.; Takei, F.; Takahashi, S. *Macromolecules* **2004**, *37*, 8204. (q) Hourani, R.; Whitehead, M. A.; Kakkar, A. *Macromolecules* **2004**, *41*, 508. (r) Yam, V. W. W.; Zhang, L.; Tao, C.-H.; Wong, K. M. C.; Cheung, K.-K. *J. Chem. Soc., Dalton Trans.* **2001**, 1111. (s) Werner, H.; Bachmann, P.; Laubender, M.; Gevert, O. *Eur. J. Inorg. Chem.* **1998**, 1217.

(10) Heterometallic systems with 1,3,5-triethynylbenzene:(a) Vicente, J.; Chicote, M. T.; Alvarez-Falcon, M. M. *Organometallics* **2005**, *24*, 2764. (b) Chong, S. H. F.; Lam, S. C. F.; Yam, V. W. W.; Zhu, N.; Cheung, K. K.; Fathallah, S.; Costuas, K.; Halet, J. F. *Organometallics* **2004**, *23*, 4924. (c) Long, N. J.; Martin, A. J.; White, A. J. P.; Williams, D. J.; Fontani, M.; Laschi, F.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3387. (d) Long, N. J.; Martin, A. J.; De Biani, F. F.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2017. (e) Powell, C. E.; Cifuentes, M. P.; Humphrey, M. G.; Willis, A. C.; Morrall, J. P.; Samoc, M. *Polyhedron* **2007**, *26*, 284.

(11) (a) Harriman, A.; Hissler, M.; Trompette, O.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 2516. (b) Chiorboli, C.; Indelli, M. T.; Scandola, F. *Top. Curr. Chem.* **2005**, *257*, 63. (c) Guo, F.; Kim, Y.-G.; Reynolds, J. R.; Schanze, K. S. *Chem. Commun.* **2006**, 1887. (d) Revadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (e) Otsuki, J.; Akasaka, T.; Araki, K. *Coord. Chem. Rev.* **2008**, *252*, 32.

(12) (a) Fischer, M.; Lieser, G.; Rapp, A.; Schnell, I.; Mamdouh, W.; De Feyter, S.; De Schryver, F. C.; Hoeger, S. *J. Am. Chem. Soc.* **2004**, *126*, 214. (b) Bunz, U. H. F. *Top. Curr. Chem.* **1999**, *201*, 131.
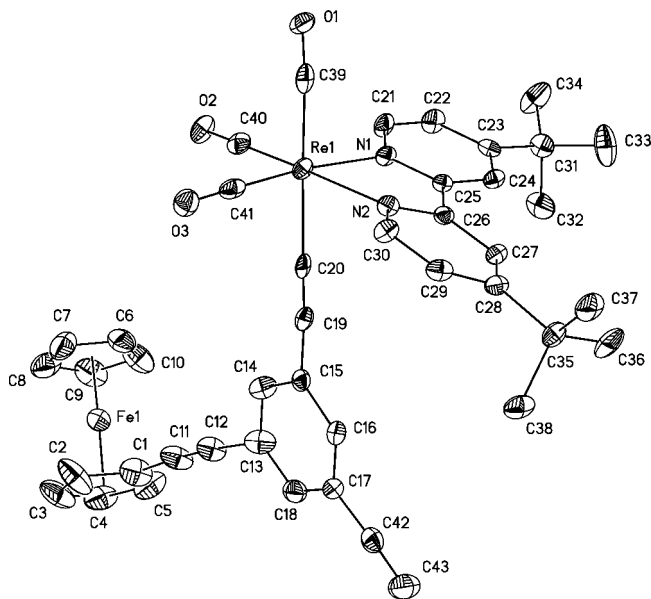
(13) Chase, P. A.; Klein Gebbink, R. J. M.; van Koten, G. *J. Organomet. Chem.* **2004**, *689*, 4016.

(14) (a) Long, N. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 21. (b) Fillaut, J.-L.; Perruchon, J.; Blanchard, P.; Roncali, J.; Golhen, S.; Allain, M.; Migalsaka-Zalas, A.; Kityk, I. V.; Sahraoui, B. *Organometallics* **2005**, *24*, 687.

(15) (a) Robertson, N.; Mc Gowan, G. A. *Chem. Soc. Rev.* **2003**, *32*, 96. (b) Caroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 4379. (c) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791. (d) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.

(16) For example see:(a) Debroy, P.; Roy, S. *Coord. Chem. Rev.* **2007**, *251*, 203. (b) Special issue, 50th Anniversary of the Discovery of Ferrocene: *J. Organomet. Chem.* **2001**, *637−639* (Adams, R. D., Ed.), and references cited therein.

(17) (a) Yam, V. W. W. *Chem. Commun.* **2001**, 789. (b) Yam, V. W. W.; Wong, K. M. C.; Chong, S. H. F.; Lau, V. C. Y.; Lam, S. C. F.; Zhang, L.; Cheung, K. K. *J. Organomet. Chem.* **2003**, *670*, 205. (c) Yam, V. W. W.; Lau, V. C. Y.; Cheung, K. K. *Organometallics* **1995**, *14*, 2749. (d) Hevia, E.; Perez, J.; Riera, V. *Inorg. Chem.* **2002**, *41*, 4673.

Figure 1. Molecular structure (ORTEP, 30% probability level) of **6**. Only one of the two independent molecules of **6** is presented with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C11−C12, 1.192(3); C19−C20, 1.158(4); C21−C22, 1.154(3); Fe1-D1, 1.652(2); Fe1-D2, 1.647(2); C1−C11−C12, 176.1(2); C11−C12−C13, 176.0(2); C15−C19−C20, 179.7(3); C17−C21−C22, 179.6(3) (D1 = centroid of C1−C5, D2 = centroid of C6−C10).

on silica gel in 65% yield (Experimental Section). The only byproduct in this reaction could be identified as 1-(FcC≡C)-3,5-[(*t*Bu₂bpy)(CO)₃ReC≡C]₂C₆H₃ (**9**), which could be isolated in low yield (Experimental Section).

Complex **8** gave a satisfactory elemental analysis and was characterized by ¹H, ¹³C{¹H}, and IR spectroscopy. The structure of **8** in the solid state was determined by single-crystal X-ray diffraction. The identity of **9** was evidenced by IR and ¹H NMR spectroscopy as well as mass spectrometry.

Most characteristic in the IR spectra of **8** and **9** is the appearance of two $\nu_{C\equiv C}$ absorptions at 2217 and 2093 cm⁻¹ (**8**) or at 2213 and 2089 cm⁻¹ (**9**), which can be assigned to the FcC≡C and ReC≡C units, respectively. However, for the noncoordinated HC≡C entity in **8** only the respective $\nu_{\equiv C-H}$ vibration is observed at 3291 cm⁻¹, while the C≡C stretching frequency is concealed by the strong carbonyl vibrations (1884, 1901, 2003 cm⁻¹).

The ¹H NMR spectrum of **8** reveals a singlet at 2.93 ppm, corresponding to the acetylenic proton. Due to the unsymmetrical substitution, the aryl protons on the 2,4,6-positions of the central phenylene ring in **8** were found to show three separated pseudotriplets with $J_{HH} = 1.6$ Hz, while for complex **9** these protons evince a doublet and a triplet. The protons of the ferrocene and bipyridyl units give typical resonances with the anticipated chemical shifts and coupling patterns (Experimental Section).

Single crystals of **6** and **8** suitable for X-ray diffraction studies could be grown from a diethyl ether/*n*-hexane solution (2:1) of **6** or by slow vapor diffusion of *n*-hexane into a dichloromethane solution containing **8**. Figures 1 and 2 show the perspective drawings of **6** and **8** together with the atom-numbering scheme.

Molecule **6** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit. The difference between these two molecules is the orientation of the ferrocene moiety relative to the central phenylene ring. The interplanar angles between the substituted cyclopentadienyl ring and the C₆H₃ entity are found to be 86.32(0.08)° and 3.64(0.16)°. The ferrocene unit shows an eclipsed conformation (3.94(6)°) with characteristic Fe1−D1 and Fe1−D2 (D1 = centroid of C1−C5, D2 = centroid of C6−C10) separations.[9a,16] The acetylide unit is, with angles of 176.1(2)° (C1−C11−C12) and

Figure 2. Molecular structure (ORTEP, 30% probability level) of **8** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Fe1–D1, 1.638(5); Fe1–D2, 1.633(5); C11–C12, 1.179(15); C42–C43, 1.197(12); C19–C20, 1.179(7); Re1–C20, 2.151(6); Re1–C39, 1.952(7); Re1–C40, 1.917(6); Re1–C41, 1.889(7); C39–O1, 1.165(6); C40–O2, 1.161(6); C41–O3, 1.189(6); Re1–N1, 2.173(4); Re1–N2, 2.177(4); C1–C11–C12, 176.3(13); C11–C12–C13, 175.9(15); C17–C42–C43, 176.6(16); C15–C19–C20, 173.8(5); C19–C20–Re1, 176.2(4); N1–Re1–N2, 73.59(15) (D1 = centroid of C1–C5, D2 = centroid of C6–C10).

176.0(2)° (C11–C12–C13), linear with a typical C≡C bond distance of 1.179(15) Å.

Complex **8** crystallizes in the monoclinic space group $P2_1/n$. The FcC≡C and HC≡C units and a part of one *tert*-butyl group are disordered and have been refined to split occupancies of 0.61/0.39 (Fe1, C1–C11), 0.64/0.36 (C42, C43), and 0.70/0.30 (C32, C34). The structure of **8** shows a somewhat distorted octahedral geometry around Re1 with three carbonyl ligands arranged in a facial fashion and Fe1 as part of a sandwich structure. The N1–Re1–N2 angle, at 73.59(15)°, is significantly less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridyl (Figure 2). Similar observations were found in, for example, 1-[(bpy′)(CO)₃ReC≡C]-3,5-(HC≡C)₂C₆H₃ (bpy′ = 4,4′-dimethyl-2,2′-bipyridyl).[10b] The bond distances of the three alkynyl units are 1.179(15) (C11–C12), 1.179(7) (C19–C20), and 1.197(12) Å (C42–C43) (Figure 2), which are comparable to those found for other triethynylbenzene metal-containing molecules.[9,10] The Re1–C20–C19–C15 unit is almost linear (Re1–C20–C19, 176.2(4)°; C15–C19–C20, 173.8(5)°), as found in related rhenium(I) acetylides.[10b,17]

Complex **8** possesses a free ethynyl moiety that provides a further reactive site and therefore should have a great potential to introduce a third transition metal building block. Thus, the reaction behavior of the disubstituted iron−rhenium assembly **8** toward diverse transition metal complexes was studied. However, it was found that treatment of **8** with [(Ph₃P)AuCl] resulted in a ligand exchange to afford [(ᵗBu₂bpy)(CO)₃ReCl] along with so far undefined species.

The synthesis of organometallic π-tweezer-based copper (I) acetylides is possible by the reaction of [{[Ti](μ-σ,π-C≡CSiMe₃)₂}CuCH₃] ([Ti] = (η⁵-C₅H₄SiMe₃)₂Ti) with CH-

acidic alkynes.[18] Nevertheless, attempts to obtain 1-(FcC≡C)-3-[(ᵗBu₂bpy)(CO)₃ReC≡C]-5-[{[Ti](μ-σ,π-C≡CSiMe₃)₂}CuC≡C]C₆H₃ by reacting **8** with [{[Ti](μ-σ,π-C≡CSiMe₃)₂}CuCH₃] in tetrahydrofuran at room temperature failed, presumably due to the steric bulkiness of the bis(alkynyl)titanocene and the [(ᵗBu₂bpy)(CO)₃Re] fragments.

In contrast, the preferred synthetic method for the preparation of heterotrimetallic compounds was accomplished by the addition of [(η⁵-C₅H₅)(Ph₃P)₂RuCl] (**10**) to **8** in a 1:1 methanol/dichloromethane mixture at 25 °C in the presence of [NH₄]PF₆ and KOᵗBu, respectively (Scheme 2). The Ru−C≡CR bond formation is generally done in two separate steps, giving first the vinylidene complex, which after deprotonation affords the appropriate ruthenium acetylide. In case of the reaction of **10** with **8** we found that the simultaneous addition of [NH₄]PF₆ and the base KOᵗBu gave significantly better yields of **12**. The isostructural osmium(II) complex **13** could be prepared by the reaction of **8** with [(η⁵-C₅H₅)(Ph₃P)₂OsBr] (**11**) in refluxing methanol in the presence of [NH₄]PF₆ followed by deprotonation of the vinylidene intermediate by addition of sodium metal. After appropriate workup, 1-(FcC≡C)-3-[(ᵗBu₂bpy)(CO)₃ReC≡C]-5-[(η⁵-C₅H₅)(Ph₃P)₂MC≡C]C₆H₃ (**12**, M = Ru; **13**, M = Os) could be isolated as orange solids in 63% (**12**) or 67% (**13**) yield (Experimental Section).

A possibility to introduce a platinum building block in **8** exists in the reaction of this compound with *cis*-[(PPh₃)₂PtCl₂] (**14**) in refluxing chloroform in the presence of diethyl amine.[19] To avoid the formation of the corresponding platinum bis(acetylide) complex, an excess of **14** was used. 1-(FcC≡C)-3-[(ᵗBu₂bpy)-(CO)₃ReC≡C]-5-[*trans*-Cl(Ph₃P)₂PtC≡C]C₆H₃ (**15**) could be isolated as a yellow solid in good yield after purification by column chromatography on silica gel.

Pendant nitrogen-containing ligands should be capable of coordinating to different transition metal fragments and consequently should be suitable for the preparation of transition metal assemblies of higher nuclearity. Thus, we have been interested in introducing an NCN-pincer unit (NCN = [C₆H₃(CH₂NMe₂)₂-2,6]⁻) as chelating ligand in **8**. Therefore, complex **8** was reacted with equimolar amounts of I-1-C₆H₂(CH₂NMe₂)₂-3,5-Br-4 (**16**) under typical Sonogashira cross-coupling conditions (Scheme 2 and Experimental Section).[20] The respective heterobimetallic NCN-pincer molecule 1-(FcC≡C)-3-[(ᵗBu₂bpy)(CO)₃ReC≡C]-5-[Br-4-C₆H₂(CH₂NMe₂)₂-3,5-C≡C-1]C₆H₃ (**17**) was formed in good yield along with traces of acetylide-coupled **18** (Scheme 2). In **18** two 1-(FcC≡C)-3-[(ᵗBu₂bpy)(CO)₃ReC≡C]C₆H₃ fragments are connected via a linear butadiyne unit. A practical method to extend the conjugation of ethynylphenyl systems is given by the oxidative homocoupling of the appropriate terminal acetylene by the Eglinton−Glaser reaction.[21] Thus, complex **18** could directly be prepared in good yield by the oxidative

(18) (a) Frosch, W.; Back, S.; Rheinwald, G.; Köhler, K.; Pritzkow, H.; Lang, H. *Organometallics* **2000**, *19*, 4016. (b) Frosch, W.; Back, S.; Lang, H. *Organometallics* **1999**, *18*, 5725. (c) Frosch, W.; Back, S.; Rheinwald, G.; Koehler, K.; Zsolnai, L.; Huttner, G.; Lang, H. *Organometallics* **2000**, *19*, 5769.

(19) (a) Furlani, A.; Licoccia, S.; Russo, M. V.; Chiesi Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1984**, 2197. (b) D'Amato, R.; Furlani, A.; Colapietro, M.; Portalone, G.; Casalboni, M.; Falconieri, M.; Russo, M. V. *J. Organomet. Chem.* **2001**, *627*, 13. (c) D'Amato, R.; Fratoddi, I.; Cappotto, A.; Altamura, P.; Delfini, M.; Bianchetti, C.; Bolasco, A.; Polzonetti, G.; Russo, M. V. *Organometallics* **2004**, *23*, 2860.

(20) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

(21) (a) Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225. (b) Stang, P. J.; Diederich, F. *Modern Acetylene Chemistry*; VCH: Weinheim, 1995. (c) Glaser, G. *Chem. Ber.* **1869**, *2*, 422. (d) Glaser, G. *Liebigs Ann. Chem.* **1870**, 159.
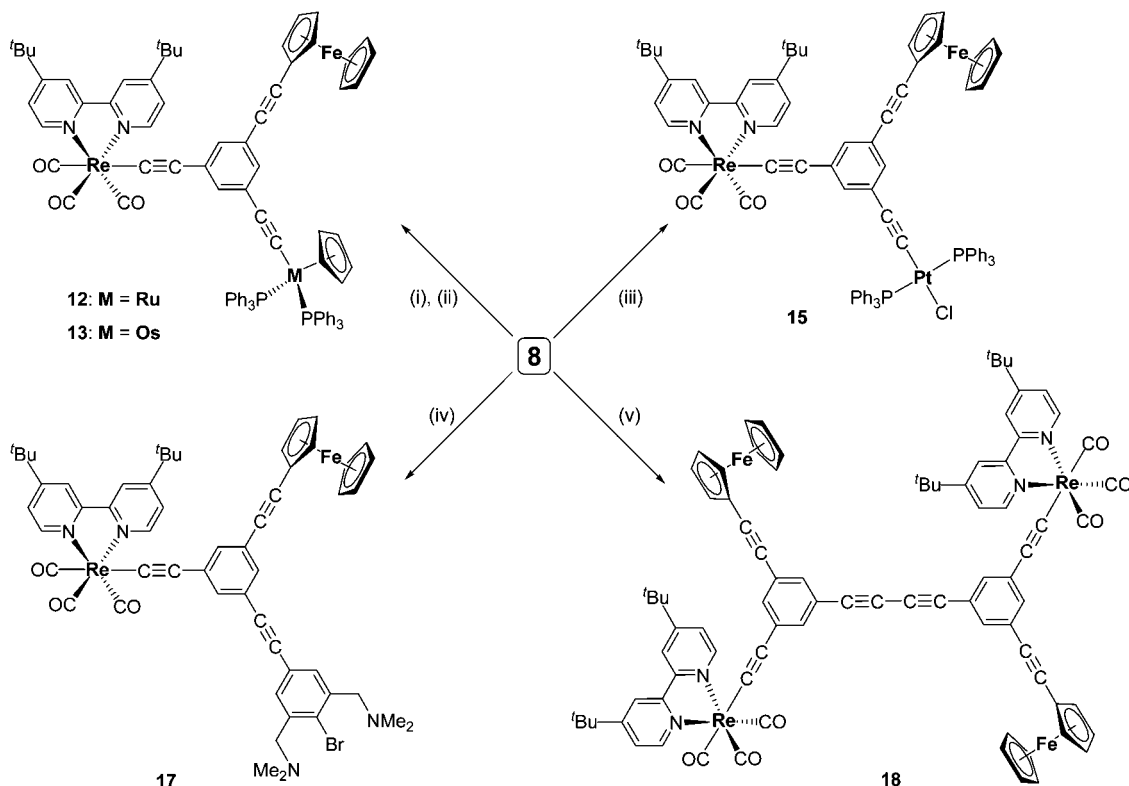
[a] (i) [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$RuCl] (10), [NH$_4$]PF$_6$, KO^{t}Bu, CH$_2$Cl$_2$/MeOH, 25 °C; (ii) 1. [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$OsBr] (11), [NH$_4$]PF$_6$, MeOH, reflux, 2. Na, MeOH, 25 °C; (iii) *cis*-[(PPh$_3$)$_2$PtCl$_2$] (14), CHCl$_3$/HNEt$_2$, reflux; (iv) 1-I-NCN-4-Br (16), [(PPh$_3$)$_2$PdCl$_2$]/[CuI], HN^{i}Pr$_2$, 35 °C; (v) [CuCl], O$_2$, pyridine, 40 °C.

dimerization of **8** catalyzed by cuprous(I) chloride in pyridine under an oxygen atmosphere (Scheme 2).

The standard procedure involving lithiation–transmetalation for the synthesis of palladium- and platinum-NCN-pincers,[22] however, could not be applied for the preparation of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(XM-4-C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-3,5-C≡C-1)C$_6$H$_3$ (M = Pd, Pt; X = Cl, Br), since lithiation of **17** appeared not to be possible. Another possibility to introduce transition metals in NCN-pincer chemistry is given by the oxidative addition of carbon–halide bonds to low-valent transition metals, i.e., [Pd$_2$(dba)$_3$×CHCl$_3$] (dba = dibenzylidene acetone).[23] For the preparation of isostructural platinum NCN-pincer complexes the platinum source [Pt(tol)$_2$(SEt$_2$)]$_2$ (tol = 4-tolyl) can be used.[23] Thus, we reacted **17** with [Pd$_2$(dba)$_3$× CHCl$_3$] and [Pt(tol-4)$_2$(SEt$_2$)]$_2$, respectively, in benzene or toluene solutions at different temperatures. It was found that the addition of the Pd and Pt starting materials to **17** did not lead to the formation of the desired compounds, which was evidenced by NMR spectroscopic measurements, e.g., the introduction of platinum into the NCN-pincer unit leads to the appearance of typical platinum satellites for the resonance signals of the CH$_2$NMe$_2$ arms, which, however, could not be observed.

The IR spectra of **12**, **13**, and **15** exhibit next to the weak Fc*C*≡*C* and Re*C*≡*C* and intense CO vibrations a medium-

intensity band at 2064 (**12**), 2065 (**13**), and 2116 (**15**), respectively, corresponding to the $\nu_{C≡C}$ absorptions of the Ru, Os, and Pt metal alkynyls, which are diagnostic and represent a useful monitoring tool.[19,24,25] The additionally expected C≡C stretching vibrations in **17** and **18** could not be located, since they are obviously concealed by the strong carbonyl bands. Nevertheless, the formation of both species could be followed to completion by disappearance of the C≡C–H band (3291 cm^{-1}).

The ^{1}H NMR spectroscopic properties of **12**, **13**, **15**, **17**, and **18** correlate with their formulations as heterobi- or heterotri-metallic complexes (Experimental Section). Characteristic of all complexes is the singlet for the ^{t}Bu groups at 1.45 ppm, the typical ferrocene resonance signals between 4.15 and 4.45 ppm, the bipyridine protons with the respective coupling pattern, and a complicated series of multiplets for the aromatic protons of the phenyl groups present. The cyclopentadienyl ring at ruthenium and osmium gives a singlet at 4.26 (**12**) or 4.34 ppm (**13**). The aryl protons of the central phenylene ring were found as three separated pseudotriplets showing an upfield shift upon

(22) (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (b) Lagunas, M. C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731. (c) Back, S.; Lutz, M.; Spek, A. L.; Lang, H.; van Koten, G. *J. Organomet. Chem.* **2001**, *620*, 227.

(23) Rodríguez, G.; Albrecht, M.; Schoenmaker, J.; Ford, A.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2002**, *124*, 5127.

(24) (a) Paul, F.; Ellis, B. G.; Bruce, M. I.; Toupet, L.; Roisnel, T.; Costuas, K.; Halet, J.-F.; Lapinte, C. *Organometallics* **2006**, *25*, 649. (b) Bruce, M. I.; Low, P. J.; Hartl, F.; Humphrey, P. A.; de Montigny, F.; Jevric, M.; Lapinte, C.; Perkins, G. J.; Roberts, R. L.; Skelton, B. W.; White, A. H. *Organometallics* **2005**, *24*, 5241. (c) Sato, M.; Kawata, Y.; Shintate, H.; Habata, Y.; Akabori, S.; Unoura, K. *Organometallics* **1997**, *16*, 1693. (d) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **2002**, *650*, 141. (e) Powell, C. E.; Cifuentes, M. P.; McDonagh, A.; Hurst, S. K.; Lucas, N. T.; Delfs, C. A.; Stranger, R.; Humphrey, M. G.; Houbrechts, S.; Asselberghs, I.; Persoons, A.; Hockless, D. C. *Inorg. Chim. Acta* **2003**, *352*, 9.

(25) Xia, H. P.; Ng, W. S.; Ye, J. S.; Li, X. Y.; Wong, W. T.; Lin, Z.; Yang, C.; Jia, G. *Organometallics* **1999**, *18*, 4552.
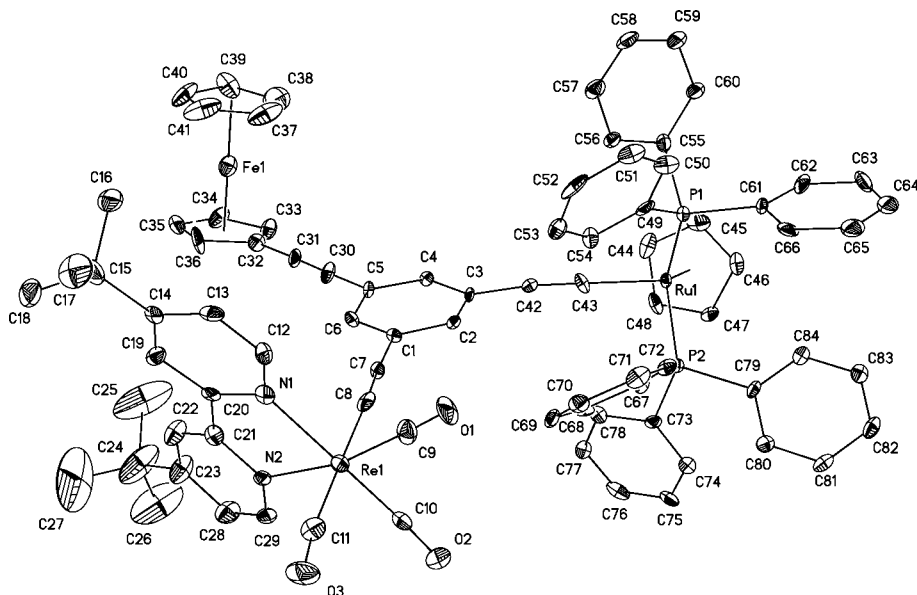
Figure 3. Molecular structure (ORTEP, 30% probability level) of **12**. Only one of the two independent molecules of **12** is presented with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Fe1−D1, 1.667(7); Fe1−D2, 1.671(8); C30−C31, 1.193(17); Re1−N1, 2.169(12); Re1−N2, 2.184(10); Re1−C8, 2.096(14); C7−C8, 1.234(17); Re1−C9, 1.922(15); Re1−C10, 1.874(19); Re1−C11, 1.939(15); C9−O1, 1.132(16); C10−O2, 1.175(19); C11−O3, 1.178(16); Ru1−D3, 1.878(6); Ru1−P1, 2.289(4); Ru1−P2, 2.276(3); Ru1−C43, 1.995(12); C42−C43, 1.223(16); C5−C30−C31, 178.1(16); C30−C31−C32, 178.4(16); N1−Re1−N2, 74.5(4); Re1−C8−C7, 174.3(11); C1−C7−C8, 176.3(13); P1−Ru1−P2, 100.46(11); Ru1−C43−C42, 173.8(10); C3−C42−C43, 169.2(12) (D1 = centroid of C32−C36, D2 = centroid of C37−C41, D3 = centroid of C44−C48).

the coordination of the alkynyl unit to Ru(II), Os(II), or Pt(II), which is most distinctive in **15**, where the protons next to the [(PPh$_3$)$_2$(Cl)PtC≡C] group appear at 5.77 and 5.80 ppm. Such an upfield shift in the C$_6$H$_3$ signals in **12**, **13**, and **15** compared to **8** may be suggestive of the electron-richness of the appropriate transition metal moieties leading to a reduced electron donation from the alkynyl unit.

The ^{31}P{^{1}H} NMR spectra of **12** and **13** show a singlet indicative of equivalent phosphine environments. The spectrum of the platinum complex **15** presents the expected signal, which consists of three lines in the ratio of 17:66:17 because of the coupling with ^{195}Pt. The magnitude of $^1J_{31P195Pt}$ is known to act as a useful probe of the geometry of any present isomer in d^8-electron-configured square-planar Pt(II) complexes.[26] The $^1J_{31P195Pt}$ value of **15** is, at 2657 Hz, in agreement with the values found in other square-planar platinum complexes with *trans*-geometry.[19,27]

For complexes **12**, **13**, **15**, **17**, and **18** electrospray ionization mass spectrometric investigations indicated the presence of the appropriate molecular ion [M + H]$^+$ with characteristic isotope distribution patterns. Characteristic for these compounds is the formation of fragments, such as [(^{t}Bu$_2$bpy)(CO)$_3$Re]$^+$ (539.1), [(C$_5$H$_5$)(PPh$_3$)$_2$Ru(CO)]$^+$ (719.0), and [(C$_5$H$_5$)(PPh$_3$)$_2$Os(CO)]$^+$ (809.1).[28]

Single crystals of heterotrimetallic **12**, **13**, and **15** suitable for X-ray structure analysis could be obtained by layering chloroform solutions of **12**, **13**, or **15** with *n*-pentane. Figures 3–5 depict the perspective drawings of the respective complexes

together with the atomic numbering scheme and selected bond distances (Å) and angles (deg). The crystallographic data are summarized in Table 5 (Experimental Section).

Complexes **12** and **13** are quite similar and both crystallize in the monoclinic space group *P*2/*c* with two independent molecules and three solvent molecules of CHCl$_3$ in the asymmetric unit. Figures 3 and 4 represent only one of the two molecules. In both crystal structures the second molecule shows a disorder of a part of the C≡C−Fc unit, which has been refined to split occupancies of 0.60/0.40 (**12**) and 0.59/0.41 (**13**). In addition, the disorder of one *tert*-butyl group in **13** has been refined to split occupancies of 0.66/0.34 (C15−C18). For complex **12** this disorder could not successfully be refined.

In contrast, complex **15** crystallizes in the monoclinic space group *P*2$_1$/*n* together with one molecule of CHCl$_3$. Thereby the *tert*-butyl groups and the chloroform show a disorder that has been refined to split occupancies of 0.65/0.35 (C8−C10), 0.50/0.50 (C16−C19), and 0.62/0.38 (C80,Cl2−Cl4).

As typical of other ferrocene complexes the Fe−D1 and Fe−D2 separations in **12**, **13**, and **15** are found between 1.640(3) and 1.699(8) Å.[9a,16] The two cyclopentadienyl ligands are thereby rotated by 2.18(0.60)° (**12**), 4.04(0.56)° (**13**), and 3.43(0.46)° (**15**) with respect to each other, which verifies an almost eclipsed conformation. The Fc−C≡C−C$_{Ph}$ units are, as expected, essentially linear with typical C≡C separations.

The structures of **12**, **13**, and **15** show a slightly distorted octahedral geometry around Re1 with three carbonyl ligands in a facial fashion. The N1−Re1−N2 bond angles are, at 74.5(4)°, 74.4(4)°, and 74.29(16)°, significantly less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridyl ligand. The Re−C≡C−C$_{Ph}$ units confirm, with bond angles of 170.6(10)−177.3(6)°, an almost linear arrangement. Furthermore, the C≡C distances are typical for rhenium metal acetylides. Compared to the Re−C$_{CO}$ separations the Re−C$_{C≡C}$ distances are somewhat longer, which is indicative for little or no significant π-back-bonding to the acetylide unit.

(26) Pregosin, P. S. Kunz, R. W. Eds. *^{31}P- and ^{13}C-NMR of Transition Metal Phosphine Complexes*; Springer Verlag" Berlin, 1976.

(27) (a) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987. (b) Bhattacharyya, P.; Sheppard, R. N.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2393.

(28) (a) Xia, H. P.; Wu, W. F.; Ng, W. S.; Williams, I. D.; Jia, G. *Organometallics* **1997**, *16*, 2940. (b) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585, and references therein.
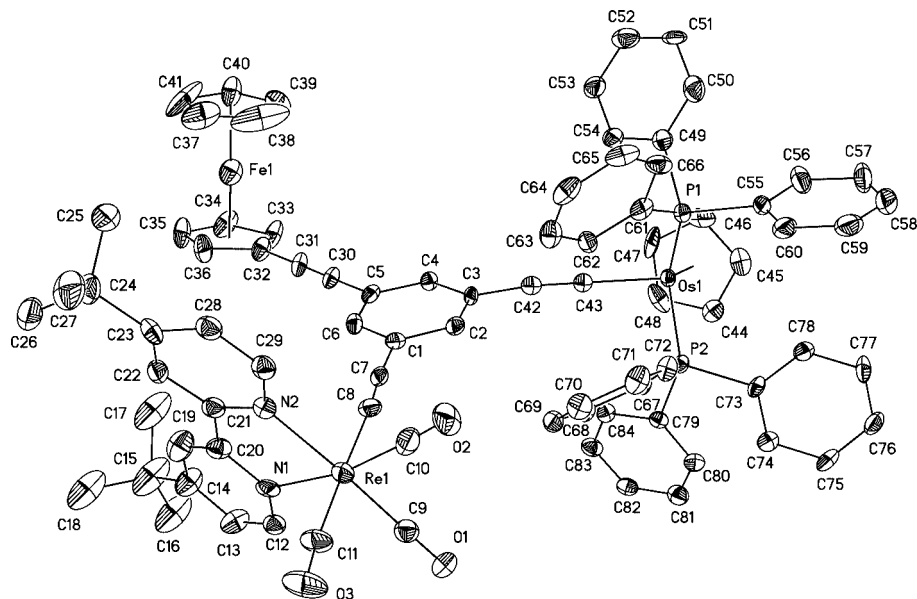
Figure 4. Molecular structure (ORTEP, 30% probability level) of **13**. Only one of the two independent molecules of **13** is presented with the atom-numbering scheme. Hydrogen atoms and three molecule of CHCl$_3$ are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Fe1−D1, 1.697(7); Fe1−D2, 1.699(8); C30−C31, 1.178(16); Re1−N1, 2.179(10); Re1−N2, 2.175(9); Re1−C8, 2.105(11); C7−C8, 1.240(15); Re1−C9, 1.913(15); Re1−C10, 1.917(15); Re1−C11, 1.958(12); C9−O1, 1.160(15); C10−O2, 1.161(16); C11−O3, 1.127(15); Os1-D3, 1.886(5); Os1−P1, 2.285(3); Os1−P2, 2.279(3); Os1−C43, 2.020(11); C42−C43, 1.208(15); C5−C30−C31, 178.8(14); C30−C31−C32, 179.1(16); N1−Re1−N2, 74.4(4); Re1−C8−C7, 170.6(10); C1−C7−C8, 174.1(12); P1−Os1−P2, 99.92(10); Os1−C43−C42, 176.3(9); C3−C42−C43, 170.8(11) (D1 = centroid of C32−C36, D2 = centroid of C37−C41, D3 = centroid of C44−C48).
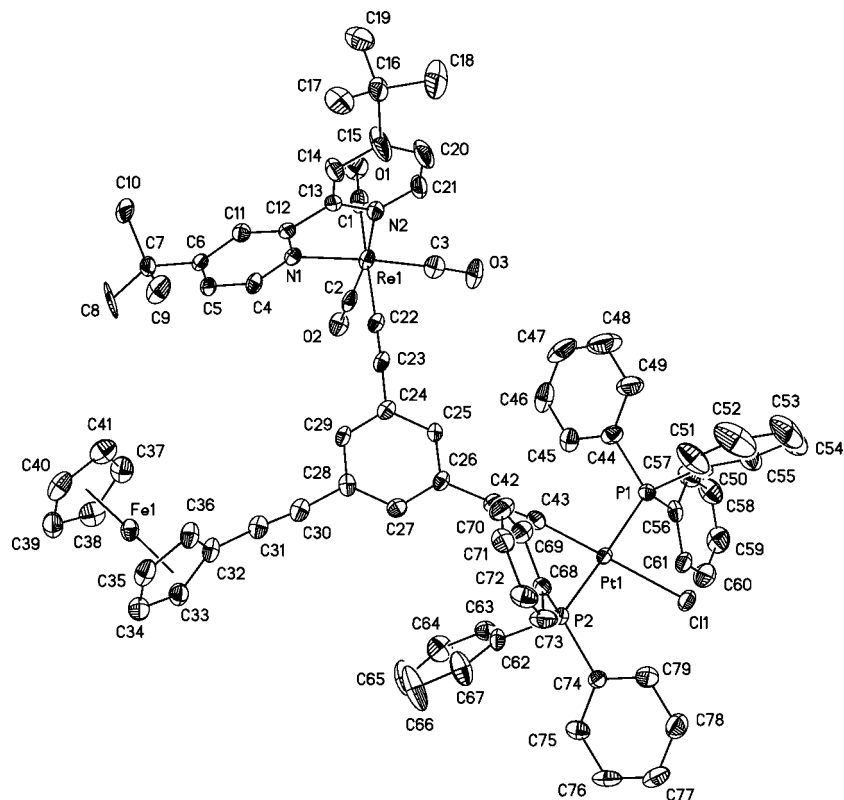
Figure 5. Molecular structure (ORTEP, 50% probability level) of **15** with the atom-numbering scheme. Hydrogen atoms and one CHCl$_3$ solvent molecule are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Fe1−D1, 1.640(3); Fe1−D2, 1.651(3); C30−C31, 1.199(8); Re1−N1, 2.178(4); Re1−N2, 2.177(5); Re1−C22, 2.114(5); C22−C23, 1.214(7); Re1−C1, 1.963(6); Re1−C2, 1.920(7); Re1−C3, 1.918(6); C1−O1, 1.144(7); C2−O2, 1.145(7); C3−O3, 1.153(7); Pt1−Cl1, 2.3553(13); Pt1−P1, 2.3124(13); Pt1−P2, 2.3154(13); Pt1−C43, 1.959(5); C42−C43, 1.197(7); C28−C30−C31, 174.1(6); C30−C31−C32, 173.3(6); N1−Re1−N2, 74.29(16); Re1−C22−C23, 177.2(5); C22−C23−C24, 177.3(6); P1−Pt1−P2, 173.09(5); Cl1−Pt1−C43, 179.29(16); Pt1−C43−C42, 173.2(5); C26−C42−C43, 178.9(6) (D1 = centroid of C32−C36, D2 = centroid of C37−C41).

Table 1. Electrochemical Data for 6, 8, 12, 13, 15, and 18[a]

compd	bpy/bpy[•−] E_0 (ΔE_p)	[Fe(II)]/[Fe(III)] E_0 (ΔE_p)	[Re(I)]/[Re(II)] $E_{p,ox}$	[M(II)]/[M(III)] $E_{p,ox}$	$E_{p,ox}/E_0$ (ΔE_p)
6		0.15 (0.12)			
8	−2.07 (0.14)	0.13 (0.105)	0.64		1.37
18	−2.05 (0.115)	0.13 (0.085)	0.64		
12	−2.08 (0.13)	0.13 (0.085)	0.67	0.05	1.09/1.33
13	−2.09 (0.13)	0.14 (0.105)	0.64	−0.10	0.86 (0.19)/1.44
15	−2.07 (0.125)	0.11 (0.09)	0.61		1.19/1.39

[a] Cyclic voltammograms from 10^{-3} M solutions in dichloromethane at 25 °C with [n-Bu$_4$N]PF$_6$ (0.1 M) as supporting electrolyte, scan rate = 0.10 V s^{-1}. All potentials are given in V and are referenced to the FcH/FcH$^+$ redox couple (FcH = (η^5-C$_5$H$_5$)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 0.10 V)).[32,33] Detailed experimental conditions are listed in the Experimental Section.

The geometries of the isostructural [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$M] (M = Ru, Os) building blocks in **12** and **13** are similar to those of many previously reported examples.[24,25,29] Both complexes have pseudotetrahedral environments about the metal centers with P1−M−P2 angles of 100.46(11)° (**12**) and 99.92(10)° (**13**). The M−P distances range between 2.276(3) and 2.289(4) Å, and the average M−Cp distances amount to 1.878(6) (**12**) and 1.886(5) Å (**13**). The alkynyl moieties are, as expected, linear with angles between 169.2(12)° and 176.3(9)° and typical C≡C separations.[24,25,29]

As typical of metals with d^8 electron configuration, the platinum(II) possesses a slightly distorted square-planar coordination geometry (rms deviation 0.0721 Å), as can be seen from the angles around Pt1 (e.g., P1−Pt1−P2, 173.09(5)°) with a linear *trans*-oriented C$_{Ph}$−C≡C−Pt−Cl arrangement (C26−C42−C43, 178.9(6)°; Pt1−C43−C42, 173.2(5)°; Cl1−Pt1−C43, 179.29(16)°, Figure 5). The deviation from an ideal square-planar arrangement can be explained by steric interactions between the bulky groups around Pt1. A similar behavior was also observed for, e.g., *trans*-[(PEt$_2$Ph)$_2$(Cl)Pt(C≡CPh)].[30c] The C≡C separation of the alkynyl moiety is, at 1.197(7) Å, representative for platinum σ-alkynyl complexes.[30]

Electrochemical Properties. Complexes **6**, **8**, **12**, **13**, **15**, and **18** were studied by cyclic voltammetry (Table 1). By comparison of the complexes it is conspicuous that there is no significant electronic interaction between the respective metal centers. This observation is based on the substitution pattern of the central phenylene ring in 1,3- and 5-position, which is unfavorable for a communication between the metal atoms.

In all complexes the [Fe(II)]/[Fe(III)] oxidation is found to be reversible between 0.11 and 0.15 V, whereby compared to **6**, this oxidation process is facilitated due to addition of further electron-releasing transition metal entities. The [(^{t}Bu$_2$bpy)-(CO)$_3$Re] building block gives rise to at least two redox processes.[10b] In the cathodic region a quasi-reversible reduction couple is found at ca. −2.07 V, which was tentatively assigned as a bipyridyl ligand-centered reduction,[5a,17c,31] as it occurred
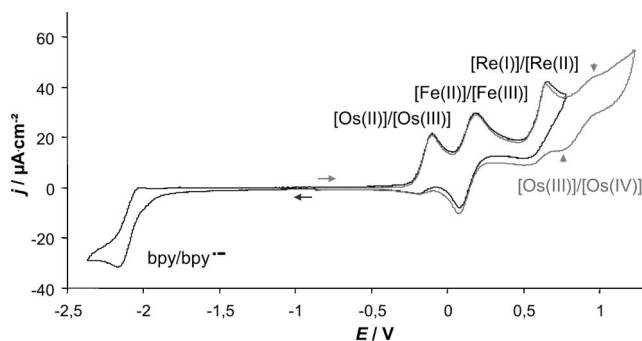

Figure 6. Cyclic voltammogram of **13** (10^{-3} M solution in dichloromethane at 25 °C with [n-Bu$_4$N]PF$_6$ (0.1 M) as supporting electrolyte, scan rate = 0.10 V s^{-1}. All potentials are referenced to the FcH/FcH$^+$ redox couple (FcH = (η^5-C$_5$H$_5$)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 0.10 V).[32,33]

Table 2. UV−Vis Absorption Spectral Data of Selected Complexes in CH$_2$Cl$_2$ at 298 K

compd	absorption λ/nm (10^{-3} ϵ/dm^3 mol^{-1} cm^{-1})
6	303 (19), 349 (4), 442 (2)
7	292 (50), 378 (21), 430 (12, sh)
8	292 (70), 350 (15, sh), 419 (8)
12	293 (72), 350 (26, sh), 419 (6)
13	292 (62), 340 (24), 430 (4)
15	292 (60), 350 (13, sh), 420 (3)
18	298 (80), 316 (62, sh), 338 (40), 420 (4)

at almost identical potential for complexes **8**, **12**, **13**, **15**, and **18**. With regard to related rhenium(I) diimine complexes the oxidation of [Re(I)] to [Re(II)] occurs at ca. 0.64 V, which means a less positive potential than in the chloro precursor **7**.[5a,17c,31] Notable is that the introduction of the *trans*-[(PPh$_3$)$_2$(Cl)Pt] fragment in **15** renders the oxidation of both the iron and the rhenium site slightly more favorable.

For the bivalent group 8 transition metals ruthenium and osmium quasi-reversible oxidation processes are observed (Table 1). The [Ru(II)]/[Ru(III)] oxidation in **12** is found at $E_{p,ox}$ = 0.05 V, whereas the oxidation of [Os(II)] to [Os(III)] in **13** occurs at a more negative potential (Table 1, Figure 6). This observation is in agreement with previous findings on related systems in which the [Os(II)]/[Os(III)] redox change is easier than the [Ru(II)]/[Ru(III)] one.[24b] Another oxidation wave found in the cyclic voltammogram of **13** at E_0 = 0.86 V can be assigned to a further oxidation of the [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Os] fragment ([Os(III)]/[Os(IV)], see Figure 6).

By going to a more positive potential, the cyclic voltammograms of complexes **8**, **12**, **13**, and **15** show additional
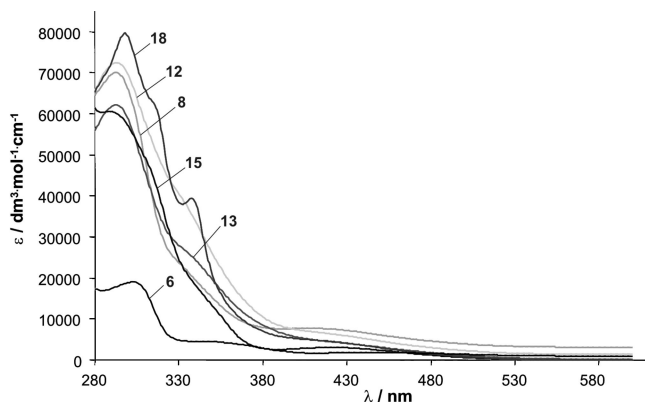
(29) (a) Matsuzaka, H.; Okimura, H.; Sato, Y.; Ishii, T.; Yamashita, M.; Kondo, M.; Kitagawa, S.; Shiro, M.; Yamasaki, M. *J. Organomet. Chem.* **2001**, *625*, 133. (b) Whittall, I. R.; Humphrey, M. G.; Hockless, D. C. R.; Skelton, B. W.; White, A. H. *Organometallics* **1995**, *14*, 3970. (c) Wu, I. Y.; Lin, J. T.; Luo, J.; Li, C. S.; Tsai, C.; Wen, Y. S.; Hsu, C. C.; Yeh, F. F.; Liou, S. *Organometallics* **1998**, *17*, 2188. (d) Cordiner, R. L.; Albesa-Jové, D.; Roberts, R. L.; Farmer, J. D.; Puschmann, H.; Corcoran, D.; Goeta, A. E.; Howard, J. A. K.; Low, P. J. *J. Organomet. Chem.* **2005**, *690*, 4908.

(30) (a) Yam, V. W. W.; Tao, C. H.; Zhang, L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 453. (b) Onitsuka, K.; Fujimoto, M.; Kitajima, H.; Ohshiro, N.; Takei, F.; Takahashi, S. *Chem.−Eur. J.* **2004**, *10*, 6433. (c) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46. (d) Zheng, Q.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, *23*, 5896.

(31) (a) Yam, V. W. W.; Chong, S. H. F.; Ko, C. C.; Cheung, K. K. *Organometallics* **2000**, *19*, 5092. (b) Yam, V. W. W.; Lau, V. C. Y.; Cheung, K. K. *Organometallics* **1996**, *15*, 1740.

(32) Ferrocene/ferrocenium redox couple: Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

(33) A conversion of given electrode potentials to the standard normal hydrogen electrode is possible: Strehlow, H.; Knoche, W.; Schneider, H. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 760.

(34) (a) Breikss, A. I.; Abruna, H. D. *J. Electroanal. Chem.* **1986**, *201*, 347. (b) Lau, V. C. Y. Ph.D. Thesis, The University of Hong Kong, 1997.

Figure 7. UV−vis spectra of selected complexes in dichloromethane at 298 K.

irreversible oxidations, which cannot indisputably be assigned to specific redox processes. By reference to complexes containing the $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru]$ redox termini the further oxidation at 1.09 V of **12** may originate from oxidation at the ruthenium center.[4j,35] The irreversible oxidation at $E_{p,ox}$ = 1.19 V (**15**) most likely arises from an oxidation at the platinum(II) center ([Pt(II)]/[Pt(III)]).[36] However, the possible involvement of a 1,3,5-triethynylbenzene ligand-centered oxidation cannot completely be excluded.[10b]

UV−Visible Absorption Spectroscopy. The electronic absorption spectrum of the mononuclear complex **6** shows a high-energy band at 303 nm and two low-energy bands at 349 and 442 nm in dichloromethane solution at room temperature (Table 2 and Figure 7). The high-energy band can be assigned to an intraligand (IL) $\pi \rightarrow \pi^*$ transition of 1,3,5-triethynylbenzene since the free ligand also absorbs strongly at similar energies. With reference to the electronic absorption of ferrocene, which shows low-energy absorptions at 326 and 438 nm, the low-energy absorption bands of **6** at 349 and 442 nm are assigned as admixtures of $d\pi(Fe) \rightarrow \pi^*(C\equiv C)$ metal-to-ligand charge transfer (MLCT) transitions.

The UV−vis spectrum of the Fe/Re complex **8** displays a similar pattern. The low-energy bands are blue-shifted and can be tentatively assigned as an admixture of $d\pi(Fe) \rightarrow \pi^*(C\equiv C)$ and $d\pi(Re) \rightarrow \pi^*(C\equiv C)$ MLCT transitions. Note that the related 1-[(bpy)(CO)$_3$ReC$\equiv$C]-4-(HC$\equiv$C)C$_6$H$_4$ also presents an absorption band centered at 420 nm.[5b] The addition of a third metal center onto the connecting ligand does not induce significant change on the low-energy absorption band, suggesting that neither the ruthenium, osmium, nor platinum units have a significant contribution to the HOMO−LUMO gap. In the case of the tetranuclear complex **18**, the high-energy bands assigned to IL $\pi \rightarrow \pi^*$ transitions are slightly more intense and the shoulders around 316 and 338 nm are almost resolved, in agreement with the extension of the organic π-system. Essentially, the UV−vis spectra of the polynuclear metal complexes consist of the sum of the absorptions of the individual building blocks, suggesting that only negligible interactions take place between the metal centers.

EPR Spectroscopy. The ferrocinium cation constitutes a very specific EPR probe. The ferrocinium cation is EPR silent and

Table 3. g Values for the Cation [8]$^+$

T (K)	$g_\parallel$	$g_\perp$	Δg^a	$g_{iso}{}^b$
77		silent		
40	4.366	1.925	2.44	2.74
20	4.348	1.925	2.42	2.73
10	4.330	1.925	2.41	2.73

^{a} $\Delta g = g_\parallel - g_\perp$. ^{b} $g_{iso} = (g_\parallel + 2g_\perp)/3$.

NMR active at liquid nitrogen temperature. The origin of this behavior was attributed to a fast spin−lattice relaxation (T_1) and a small splitting of the Kramers doublets.[37–39] At 20 K, T_1 becomes long enough to permit the observation of the EPR signal characteristic of ferrocinium ($g_\parallel$ = 4.36, $g_\perp$ = 1.30 at 20 K). The EPR spectrum of a glassy solution displays two g values characteristic of a radical with an axial symmetry because $g_x - g_y$ is too small to split the x,y EPR peak. It is noteworthy that the line width and the anisotropy of the g tensor are very large. Introduction of phenyl substituents on the C$_5$ rings reduces both the anisotropy of the signal and the line width, allowing the detection of the radicals at 77 K. It has been shown that the EPR signal is very sensitive to the perturbation of the radical associated with the introduction of aromatic substituents on the cyclopentadienyl ligands. For example, a single phenyl on one cyclopentadienyl ligand significantly modifies the values of the g tensors ($g_\parallel$ = 3.98, $g_\perp$ = 1.62).[39] This observation was for us a source of motivation for using EPR spectroscopy to study radical species *in situ* generated from **8**, **12**, **13**, **15**, and **18**, in order to detect magnetic interaction between the metal centers connected through the 1,3,5-triethynylbenzene core.

Treatment of **8** with 1 equiv of [AgOTf] in tetrahydrofuran at −60 °C provided a yellow solution, which was transferred into an EPR tube and cooled at 77 K. The EPR spectrum run at this temperature did not present any signal (Supporting Information). However, upon further cooling, a signal characteristic of a radical with an axial symmetry progressively appeared. The $g_\parallel$ and $g_\perp$ tensor components obtained for [8]$^+$ are close enough to the values already reported for ferrocinium to conclude that the oxidation of **8** takes place on the $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)Fe$ moiety (Table 3).

The perturbation induced by the 1,3,5-triethynylbenzene core and the rhenium center is without any detectable effect on $g_\parallel$, but contributes to a large increase of the $g_\perp$ tensor. However, the large line width and the weak difference between g_x and g_y do not allow the splitting of the x,y EPR peak. The thermal stability of [8]$^+$ was established by recording an identical spectrum of the same sample after storing it for approximately 1 h at 20 °C.

Complex **8** was then reacted with 2 equiv of [AgOTf] at −60 °C in tetrahydrofuran. The obtained yellow solution was transferred into an EPR tube and a spectrum was recorded at 77 K (Figure 8). The two tensor components corresponding to the ferrocinium center are now clearly visible in the spectrum, suggesting that the presence of a second unpaired electron narrows the line shape. The spectrum also displays a well-resolved signal with an axial symmetry. This signal consists of a sextet in the parallel tensor and a relatively sharp singlet for the orthogonal tensor. The sextet, which results from the hyperfine coupling of the unpaired electron with the nuclear spin of rhenium (I, ^{185,187}Re = 5/2), probes the contribution of the rhenium center on the resulting radical. The large anisotropic

(35) (a) Gao, L.-B.; Zhang, L.-Y.; Shi, L.-X.; Chen, Z.-N. *Organometallics* **2005**, *24*, 1678. (b) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949. (c) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184.

(36) Wong, W.-Y.; Lu, G.-L.; Choi, K.-H. *J. Organomet. Chem.* **2002**, *659*, 107.

(37) Fritz, H. P.; Keller, H. J.; Schwarzhans, K. E. *J. Organomet. Chem.* **1966**, *6*, 652–659.

(38) Prins, R. *Mol. Phys.* **1970**, *19*, 603–620.

(39) Prins, R.; Reinders, F. J. *J. Am. Chem. Soc.* **1969**, *91*, 4929–4931.
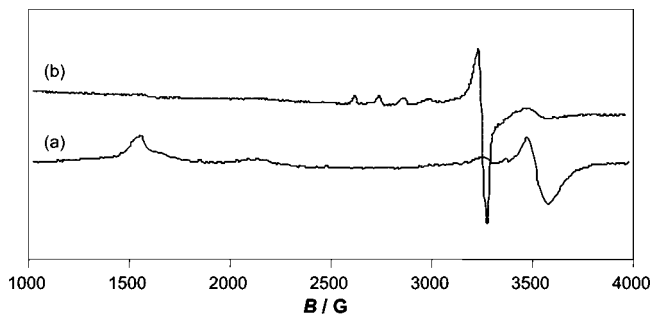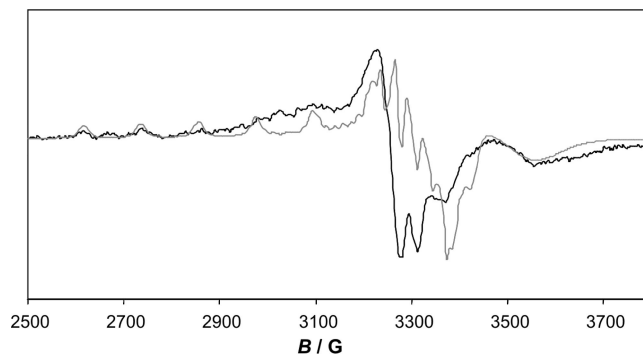
Figure 8. EPR spectrum of **8** reacted with 1 (a, 10 K) and 2 (b, 77 K) equiv of [AgOTf] in tetrahydrofuran.

Figure 9. Experimental (black) and simulated (gray) EPR spectra (77 K) of **12** reacted with 2 equiv of [AgOTf] in tetrahydrofuran (the low-field component at $g = 4.28$ has been omitted for clarity).

(Δg) and isotropic (g_{iso}) tensors indicate that the dπ(Re) orbital contribution to the g values is large and suggest that the SOMO and the doubly occupied orbitals of [**8**]$^+$ are close in energy.

The diradical that results from the double oxidation of **8** is thermally stable in tetrahydrofuran at 20 °C for at least 1 h, as established by monitoring the intensity of the EPR signal. In accord with the EPR observation, the doubly oxidized species could be regarded as a biradical with one electron centered on the ferrocinium moiety, while the second electron is located on the rhenium building block. The product resulting from the one-electron oxidation of [**8**]$^+$ possesses an EPR spectrum characteristic of a biradical involving both the ferrocinium and rhenium centers; it cannot be regarded as [**8**]$^{2+}$. Indeed, it has been demonstrated by cyclic voltammetry (*vide supra*) that the second one-electron oxidation of **8** is not chemically reversible. Therefore, as soon as [**8**]$^{2+}$ is generated in solution from the one-electron oxidation of [**8**]$^+$, it should be transformed into a new compound (i.e., [**8′**]$^{2+}$) through a chemical reaction. One can assume that the oxidation of the rhenium building block should probably be followed by the decoordination of a carbonyl group. Other chemical reactions can also be envisaged, such as the Re–C$_{sp}$ bond cleavage, but such a process will not be consistent with the observed EPR spectrum.

The respectively yellow-orange and yellow tetrahydrofuran solutions of radical [**15**]$^+$ and [**18**]$^{2+}$ obtained by treatment of **15** and **18** with 1 equiv of [AgOTf] were subjected to EPR experiments. The signal characteristic of the ferrocinium cation could not be observed in these two cases. Treatment of these solutions with a second equivalent of [AgOTf] allowed the observation of both signals corresponding to the iron and rhenium building blocks in the case of **15**, while for compound **18**, the signature of the ferrocinium center was not observed. For the doubly oxidized compounds **8**, **15**, and **18**, the g tensors corresponding to the rhenium-centered radicals are very similar, indicating that the structure of the rhenium center is not perturbed by the introduction of platinum or the duplication of the structure.

Treatment of compound **12** with 1 equiv of the silver salt [AgOTf], as described above, provided an EPR-active solution. The EPR spectrum displayed a very broad signal centered at $g = 2.05$, while the low-field component of the spectrum of the ferrocenyl radical was not detected. It is assumed that the odd electron could exchange at a fast regime with respect to the EPR time scale between the iron and ruthenium centers, in accord with the relatively close potentials of these redox centers (*vide supra*). Note that the electron transfer can take place either through the bonding or through space and does not establish the existence of electronic interactions between the metal centers. Treatment of [**12**]$^+$ with a second oxidizing reagent allowed the observation of a spectrum that essentially consists

in the addition of the signal of a radical with an axial symmetry and a radical with a rhombic geometry, attributed to the ferrocinium and the ruthenium units, respectively (Figure 9). The sample stability was good in the solvent glass, but the intensity of the signal decreases after warming of the solution for a few minutes. The three features corresponding to the three components of the g tensor of the rhombic radical are well resolved. The low-field g tensor was split into a sextet by hyperfine coupling with the rhenium nucleus. Moreover, the two high-field features are partially split into 1:2:1 triplets by hyperfine coupling with the two equivalent ^{31}P nuclei. The g tensors and the ^{185,187}Re and ^{31}P coupling were extracted by simulation (Figure 9, Table 4). The g tensors are typical of a piano-stool-centered radical[40] and are qualitatively similar to those reported for the isostructural ruthenium(III)/iron(III) complexes [(η^5-C$_5$Me$_5$)(dppe)RuC≡C-1,4-(C$_6$H$_4$)X]$^+$ and [(η^5-C$_5$Me$_5$)(dppm)FeC≡C-1,4-(C$_6$H$_4$)X]$^+$.[24a,41] The observation of the hyperfine coupling of the unpaired electron with both one rhenium and two phosphorus atoms definitely establishes that some electronic interaction between the rhenium and ruthenium building blocks takes place in [**12**]$^{2+}$.

In contrast with the other complexes, the first oxidation takes place on the osmium moiety in the case of complex **13**. Indeed, treatment of trimetallic **13** with 1 equiv of [AgOTf] under the same experimental conditions provides a spectrum corresponding to a metal-centered radical with a rhombic symmetry. The presence of additional signals in the spectrum suggests that the decomposition of the native radical cannot be completely stopped by working at low temperature. A subsequent oxidation allowed the observation of the ferrocinium signature, but the presence of too many paramagnetic impurities prevented the determination of the tensor components.

The $\Delta m_s = 2$ transitions characteristic of the triplet states of the biradicals could not be detected for any of the five doubly oxidized compounds studied. In contrast with the bi- and trinuclear iron(III) complexes [1,3-{(η^5-C$_5$Me$_5$)(dppe)FeC≡C}$_2$-(C$_6$H$_4$)][PF$_6$]$_2$ and [1,3-{(η^5-C$_5$Me$_5$)(dppe)Fe–C≡C}$_3$(C$_6$H$_3$)]-[PF$_6$]$_3$, for which through-bridge ferromagnetic metal–metal exchange interactions were observed,[9b] the spin carriers are not apparently magnetically coupled in the complexes here considered. When observed, the g tensors of the ferrocinium moiety are only weakly altered by the presence of a second radical centered on rhenium or ruthenium. However, a small decrease

(40) Rieger, P. H. *Coord. Chem. Rev.* **1994**, *135/136*, 203–286.
(41) Connelly, N. G.; Gamasa, M. P.; Gimeno, J.; Lapinte, C.; Lastra, E.; Maher, J. P.; Narvor, N. L.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1993**, 2575–2578.

Table 4. EPR Spectroscopic Data for Compounds 8, 12, 13, 15, and 18 Reacted with 1 and 2 equiv of Oxidant[a]

cmpd	1 equiv of [AgOTf]				2 equiv of [AgOTf]			
	g_1	g_2	g_3	Δg	g_1	g_2	g_3	Δg
8		silent			2.32 (122 G)	2.084		0.23
					4.262	1.913		2.35
12		$g = 2.054, \Delta H_{pp} = 700$ G			2.32 (120 G)	2.07 (32 G)	2.01 (14 G)	0.31
					4.28	1.92		2.36
13	2.12	1.985	1.895	0.22			[b]	
15		silent			2.312 (122 G)	2.082		0.23
					[c]	1.925		
18		2.084, $\Delta H_{pp} = 250$ G			2.311 (122 G)	2.084		0.23

[a] At 77 K in tetrahydrofuran glass. [b] Due to partial decomposition, the g tensors could not be extracted. [c] Not determined.

Table 5. Crystal and Intensity Collection Data for 6, 8, 12, 13, and 15

	6	**8**	**12×3 CHCl₃**	**13×3 CHCl₃**	**15×CHCl₃**
fw	334.18	871.80	3481.08	3655.31	1745.24
chemical formula	$C_{22}H_{14}Fe$	$C_{43}H_{37}FeN_2O_3Re$	$C_{171}H_{145}Cl_9Fe_2N_4O_6P_4Re_2Ru_2$	$C_{171}H_{141}Cl_9Fe_2N_4O_6Os_2P_4Re_2$	$C_{80}H_{67}Cl_4FeN_2O_3P_2PtRe$
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2/c$	$P2/c$	$P2_1/n$
a (Å)	11.814(9)	16.0242(9)	25.5669(5)	25.7473(14)	23.2869(10)
b (Å)	12.369(9)	12.0532(9)	11.3780(3)	11.4332(6)	12.9871(5)
c (Å)	12.749(10)	19.8283(16)	53.1036(11)	53.214(3)	24.1528(9)
α (deg)	71.211(13)	90	90	90	90
β (deg)	78.614(13)	101.457(5)	91.512(2)	91.527(5)	93.857(3)
γ (deg)	64.992(12)	90	90	90	90
V (Å³)	1594(2)	3753.4(5)	15442.5(6)	15659.1(15)	7288.0(5)
ρ_{calc} (g cm⁻³)	1.392	1.543	1.497	1.550	1.591
$F(000)$	688	1736	7000	7240	3448
cryst dimens (mm³)	$0.4 \times 0.3 \times 0.3$	$0.4 \times 0.1 \times 0.1$	$0.7 \times 0.6 \times 0.2$	$0.4 \times 0.1 \times 0.02$	$0.3 \times 0.05 \times 0.05$
Z	4	4	4	4	4
max., min. transmn	0.99999, 0.89342	1.00000, 0.71715	1.00000, 0.77206	1.00000, 0.09099	1.00000, 0.42374
absorp coeff (μ, mm⁻¹)	0.941	3.649	2.190	9.606	4.008
scan range (deg)	1.69 to 26.37	2.80 to 26.00	2.83 to 26.00	3.43 to 60.64	2.97 to 26.12
index ranges	$-14 \leq h \leq 14$	$-19 \leq h \leq 19$	$-30 \leq h \leq 31$	$-29 \leq h \leq 28$	$-28 \leq h \leq 28$
	$-14 \leq k \leq 15$	$-14 \leq k \leq 14$	$-12 \leq k \leq 14$	$-12 \leq k \leq 12$	$-16 \leq k \leq 16$
	$0 \leq l \leq 15$	$-24 \leq l \leq 24$	$-65 ' l \leq 53$	$-59 \leq l \leq 60$	$-29 \leq l \leq 29$
total no. of reflns	18 264	34 504	86 133	91 818	68 767
no. of unique reflns	6516	7356	30 035	23 192	14 362
R(int)	0.0285	0.0695	0.0745	0.0765	0.0331
no. of data/restraints/params	6513/0/415	7356/684/607	30 035/535/1907	23 192/334/1938	14 362/153/949
goodness-of-fit on F^2	1.042	0.966	1.122	1.032	1.108
R1,[a] wR2[a] [$I \geq 2\sigma(I)$]	0.0326, 0.0848	0.0343, 0.0625	0.1036, 0.2156	0.0695, 0.1729	0.0323, 0.0759
R1,[a] wR2[a] (all data)	0.0419, 0.0913	0.0797, 0.0776	0.1543, 0.2347	0.1007, 0.1950	0.0546, 0.0948
max., min. peak in final Fourier map (e Å⁻³)	0.284, −0.353	1.055, −0.754	5.840, −2.381	5.724, −1.373	2.390, −1.722

[a] $R1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|)$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$. $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. n = number of reflections, p = parameters used.

of the Δg tensor suggesting a small increase of the π-ligand character in the description of the SOMO was observed. Similarly the presence of the ferrocinium center is apparently not sensed by the platinum and ruthenium building blocks. Nevertheless, the presence of a second radical modifies the relaxation process of the ferrocenyl cation, allowing its observation at liquid nitrogen temperature in **8**, **12**, **13**, and **15**. In contrast, in the tetranuclear compound **18**, the signature of the ferrocinium unit could not be detected at 77 K.

Conclusion

A novel series of mono-, heterobi-, and heterotrimetallic complexes based on the 1,3,5-triethynylbenzene core have successfully been synthesized using different consecutive synthesis methods. In the thus formed organometallic molecules 1-(FcC≡C)-3-[(^{t}Bu₂bpy)(CO)₃ReC≡C]-5-(HC≡C)C₆H₃, 1-(FcC≡C)-3-[(^{t}Bu₂bpy)(CO)₃ReC≡C]-5-[(η^5-C₅H₅)(Ph₃P)₂MC≡C]C₆H₃ (M = Ru, Os), 1-(FcC≡C)-3-[(^{t}Bu₂bpy)(CO)₃ReC≡C]-5-[*trans*-(Ph₃P)₂(Cl)PtC≡C]C₆H₃, 1-(FcC≡C)-3-[(^{t}Bu₂bpy)(CO)₃ReC≡C]-5-(1-Br-NCN-4-C≡C)C₆H₃, and [1-(FcC≡C)-3-[(^{t}Bu₂bpy)(CO)₃ReC≡C]-

5-(C≡C)C₆H₃]₂, respectively (Fc = (η^5-C₅H₅)(η^5-C₅H₄)Fe; ^{t}Bu₂bpy=4,4′-di-*tert*-butyl-2,2′-bipyridyl; NCN=C₆H₂(CH₂NMe₂)₂-3,5), the appropriate transition metals are connected by a π-conjugated triethynylbenzene backbone. The X-ray crystal structures of five complexes have also been determined. Electrochemical, electron paramagnetic resonance, and UV−vis spectroscopic investigations of the heterometallic complexes show only very weak interactions between the respective metal atoms. Taken as a whole, our results indicate that the 1,3,5-triethynylbenzene is a suitable connector both to link different metal centers together and to keep their individual behavior.

Experimental Section

General Data. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, *n*-hexane, *n*-pentane, and petroleum ether were purified by distillation from sodium/benzophenone ketyl; dichloromethane and chloroform were purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

Instruments. Infrared spectra were recorded with a Perkin-Elmer FT-IR spectrometer Spectrum 1000. ^{1}H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; ^{13}C{^{1}H} NMR spectra were recorded at 62.860 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR: CDCl$_3$, $\delta = 7.26$; ^{13}C{^{1}H} NMR: CDCl$_3$, $\delta = 77.16$).[42] ^{31}P{^{1}H} NMR spectra were recorded at 101.255 MHz in CDCl$_3$ with P(OMe)$_3$ as external standard ($\delta = 139.0$, rel to H$_3$PO$_4$ (85%) with $\delta = 0.00$ ppm). ESI-TOF mass spectra were recorded using a Mariner biospectrometry workstation 4.0 (Applied Biosystems). Cyclic voltammograms were recorded in a dried cell purged with purified argon. Platinum wires served as the working electrode and the counter electrode. A saturated calomel electrode in a separated compartment served as reference electrode. For ease of comparison, all electrode potentials are converted using the redox potential of the ferrocene/ferrocinium couple FcH/FcH$^+$ (FcH = (η^5-C$_5$H$_5$)$_2$Fe, $E_0 = 0.00$ V) as reference.[32,33] Electrolyte solutions were prepared from tetrahydrofuran or dichloromethane and [^{n}Bu$_4$N]PF$_6$ (Fluka, dried in oil-pump vacuum). The appropriate organometallic complexes were added at $c = 1.0$ mM. Cyclic voltammograms were recorded on a Voltalab PGZ 100 instrument (Radiometer). UV−vis spectra were obtained on a Cary 5 spectrometer. The EPR spectra were recorded with a Bruker EMX-8/2.7 (X-band) spectrometer. Tetrahydrofuran solutions of the diamagnetic neutral complexes were reacted with [AgOTf] at −60 °C. After 15 min of stirring the solutions were transferred at this temperature in quartz EPR tubes and were immediately frozen with liquid nitrogen, and EPR spectra were run at 77 K. Microanalyses were performed with a FLASHEA 1112 Series CHN analyzer (Thermo).

Reagents. 1-Iodo-3,5-dibromobenzene,[43] ethynylferrocene,[44] trimethylsilylacetylene,[45] [(^{t}Bu$_2$bpy)(CO)$_3$ReCl],[46] [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$-RuCl],[47] [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$OsCl],[48] *cis*-[(PPh$_3$)$_2$PtCl$_2$],[49] and I-1-C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-3,5-Br-4[50] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Modified Preparation of 1-(FcC≡C)-3,5-Br$_2$C$_6$H$_3$ (3). To 500 mg (1.38 mmol) of 1-iodo-3,5-dibromobenzene (**1**) and 300 mg (1.43 mmol) of ethynylferrocene (**2**) dissolved in 50 mL of degassed diisopropylamine were added [(PPh$_3$)$_2$PdCl$_2$] (40 mg) and [CuI] (20 mg) at 0 °C. The resulting reaction mixture was stirred for 2 h at this temperature, followed by stirring overnight at 25 °C. Afterward the suspension was filtered through a pad of Celite, and the filtrate was evaporated to dryness under reduced pressure. The residual material was purified by column chromatography on alumina using a 4:1 mixture of petroleum ether and dichloromethane as eluent. The title complex was obtained from the first orange band as a red solid. Yield: 520 mg (1.17 mmol, 85% based on

1-iodo-3,5-dibromobenzene). The analytical data correspond to values reported in ref 9a.

Preparation of 1-(FcC≡C)-3,5-(Me$_3$SiC≡C)$_2$C$_6$H$_3$ (5). To a degassed diisopropylamine solution (50 mL) containing 500 mg (1.13 mmol) of 1-(FcC≡C)-3,5-Br$_2$C$_6$H$_3$ (**3**) were added 400 mg (4.08 mmol) of trimethylsilylacetylene, [(PPh$_3$)$_2$PdCl$_2$] (50 mg), and [CuI] (25 mg). The resulting suspension was stirred for 1 h at room temperature, followed by 15 h at 40 °C. After cooling it to room temperature the reaction mixture was filtered through a pad of Celite, and subsequently all volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (4:1, v/v) as eluent. After evaporation of the solvents in an oil-pump vacuum, **5** was obtained as an orange solid. Yield: 405 mg (0.85 mmol, 76% based on **3**).

Anal. Calcd for C$_{28}$H$_{30}$FeSi$_2$ (478.56): C, 70.27; H, 6.32. Found: C, 69.89; H, 6.38. Mp: 148 °C. IR (KBr, cm^{-1}): 2159 (m, $\nu_{C≡CSi}$), 2216 (m, $\nu_{C≡CFc}$). ^{1}H NMR (δ, CDCl$_3$): 0.29 (s, 18 H, Si*Me*$_3$), 4.26 (s, 5 H, C$_5$*H*$_5$), 4.27 (pt, J_{HH} = 1.8 Hz, 2 H, *H*$^\beta$/C$_5$H$_4$), 4.52 (pt, J_{HH} = 1.8 Hz, 2 H, *H*$^\alpha$/C$_5$H$_4$), 7.54 (t, J_{HH} = 1.4 Hz, 1 H, C$_6$*H*$_3$), 7.56 (d, J_{HH} = 1.4 Hz, 2 H, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (δ, CDCl$_3$): 0.1 (Si*Me*$_3$), 64.7 (*C^i*/C$_5$H$_4$), 69.3 (*CH*/C$_5$H$_4$), 70.2 (C$_5$H$_5$), 71.7 (*CH*/C$_5$H$_4$), 84.3 (*C*≡CFc), 90.2 (C≡*C*Fc), 95.7 (*C*≡CSi), 103.6 (C≡*C*Si), 123.9 (*C^i*/C$_6$H$_3$), 124.7 (*C^i*/C$_6$H$_3$), 134.3 (*CH*/C$_6$H$_3$), 134.5 (*CH*/C$_6$H$_3$).

Preparation of 1-(FcC≡C)-3,5-(HC≡C)$_2$C$_6$H$_3$ (6). 1-(FcC≡C)-3,5-(Me$_3$SiC≡C)$_2$C$_6$H$_3$ (**5**) (400 mg, 0.84 mmol) was dissolved in tetrahydrofuran (30 mL) and treated with 1.8 mL (1.80 mmol) of [^{n}Bu$_4$N]F (1.0 M in tetrahydrofuran) at 0 °C. After 30 min of stirring the cooling bath was removed and stirring was continued for 1 h. Afterward all volatiles were evaporated under reduced pressure, and the obtained residue was purified by column chromatography on silica gel using a mixture of petroleum ether/dichloromethane (3:1, v/v) as eluent. After evaporation of all volatiles the title compound was obtained as an orange solid. Yield: 260 mg (0.78 mmol, 93%).

Anal. Calcd for C$_{22}$H$_{14}$Fe (334.2): C, 79.07; H, 4.22. Found: C, 78.48; H, 4.47. Mp: 154 °C. IR (KBr, cm^{-1}): 2208 (m, $\nu_{C≡CFc}$), 3284 (s, $\nu_{≡C-H}$). ^{1}H NMR (δ, CDCl$_3$): 3.12 (s, 2 H, ≡C*H*), 4.25 (s, 5 H, C$_5$*H*$_5$), 4.27 (pt, J_{HH} = 1.8 Hz, 2 H, *H*$^\beta$/C$_5$H$_4$), 4.51 (pt, J_{HH} = 1.8 Hz, 2 H, *H*$^\alpha$/C$_5$H$_4$), 7.54 (t, J_{HH} = 1.4 Hz, 1H, C$_6$*H*$_3$), 7.59 (d, J_{HH} = 1.4 Hz, 2H, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (δ, CDCl$_3$): 64.5 (*C^i*/C$_5$H$_4$), 69.2 (*CH*/C$_5$H$_4$), 70.2 (C$_5$H$_5$), 71.7 (*CH*/C$_5$H$_4$), 78.5 (C≡*C*H), 82.1 (*C*≡CH), 84.0 (C≡*C*Fc), 90.5 (*C*≡CFc), 122.9 (*C^i*/C$_6$H$_3$), 124.9 (*C^i*/C$_6$H$_3$), 134.5 (*CH*/C$_6$H$_3$), 135.0 (*CH*/C$_6$H$_3$).

Preparation of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(HC≡C)C$_6$H$_3$ (8) and 1-(FcC≡C)-3,5-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]$_2$-C$_6$H$_3$ (9). To 350 mg (1.05 mmol) of 1-(FcC≡C)-3,5-(HC≡C)$_2$-C$_6$H$_3$ (**6**) dissolved in 60 mL of toluene was added LiN(SiMe$_3$)$_2$ (170 mg, 1.02 mmol) in a single portion at 0 °C. After 2 h of stirring at this temperature the cooling bath was removed and stirring was continued for 1 h. Then 200 mg (0.35 mmol) of [(^{t}Bu$_2$bpy)-(CO)$_3$ReCl] (**7**) was added, and the reaction mixture was heated to 100−110 °C for 5 h, while the progress of the reaction was monitored by TLC. After cooling to room temperature a few drops of ethanol were added to destroy the unreacted lithium acetylide and all volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel using a diethyl ether/petroleum ether mixture of ratio 2:1 as the eluent. After removal of the first band, which contained unreacted 1-(FcC≡C)-3,5-(HC≡C)$_2$C$_6$H$_3$ (**6**), the second band was collected. After evaporation of the solvents under reduced pressure an orange solid identified as **8** was obtained. Additionally, from a third yellow band a small amount of complex **9** was isolated. Yield: **8**, 195 mg (0.22 mmol, 65% based on **7**); **9**, 20 mg (0.114 mmol, 8% based on **7**).

8: Anal. Calcd for C$_{43}$H$_{37}$FeN$_2$O$_3$Re (871.83): C, 59.24; H, 4.28; N, 3.21. Found: C, 58.99; H, 4.46; N, 3.06. Mp: >196 °C (dec).

(42) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

(43) (a) Baxter, P. N. W. *Chem.−Eur. J.* **2003**, *9*, 5011. (b) Lustenberger, P.; Diederich, F. *Helv. Chim. Acta* **2000**, *83*, 2865.

(44) Polin, J.; Schottenberger, H. *Org. Synth.* **1996**, *13*, 262.

(45) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier-Verlag: Amsterdam, 1988; p 114.

(46) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Wrighton, M. S.; Morse, D. L.; Pdungsap, L. *J. Am. Chem. Soc.* **1975**, *97*, 2073.

(47) Joslin, F. L.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 521. (b) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601.

(48) (a) Wanandi, P. W.; Tilley, T. D. *Organometallics* **1997**, *16*, 4299. (b) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601. (c) Bruce, M. I.; Low, P. J.; Skelton, B. W.; Tiekink, E. R. T.; Werth, A.; White, A. H. *Aust. J. Chem.* **1995**, *48*, 1887.

(49) Jensen, K. A. Z. *Anorg. Allg. Chem.* **1936**, *229*, 265.

(50) Rodríguez, G.; Albrecht, M.; Schoenmaker, J.; Ford, A.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2002**, *124*, 5127.

IR (KBr, cm^{-1}): 1884, 1901, 2003 (s, ν_{CO}), 2093 (w, $\nu_{C\equiv CRe}$), 2217 (w, $\nu_{C\equiv CFc}$), 3291 (m, $\nu_{\equiv C-H}$). ^{1}H NMR (δ, CDCl$_3$): 1.47 (s, 18H, ^{t}Bu), 2.93 (s, 1 H, $\equiv CH$), 4.18 (s, 5 H, C$_5$H$_5$), 4.21 (pt, J_{HH} = 1.8 Hz, 2 H, H^β/C$_5$H$_4$), 4.41 (pt, J_{HH} = 1.8 Hz, 2 H, H^α/C$_5$H$_4$), 6.96 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.06 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.16 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.46 (dd, $^3J_{H5H6}$ = 5.8 Hz, $^4J_{H5H3}$ = 1.9 Hz, 2 H, $H5$/^{t}Bu$_2$bpy), 8.09 (d, J_{H3H5} = 1.9 Hz, 2 H, $H3$/^{t}Bu$_2$bpy), 8.97 (d, J_{H6H5} = 5.8 Hz, 2 H, $H6$/^{t}Bu$_2$bpy). ^{13}C{^{1}H} NMR (δ, CDCl$_3$): 30.5 (CH$_3$), 35.7 (C(CH$_3$)$_3$), 65.1 (C^i/C$_5$H$_4$), 68.9 (CH/C$_5$H$_4$), 70.1 (C$_5$H$_5$), 71.5 (CH/C$_5$H$_4$), 76.9 (C$\equiv$CH), 83.1 (C$\equiv$CH), 84.9 (C$\equiv$CFc), 88.5 (C$\equiv$CFc), 104.1 (C$\equiv$CRe), 119.4 (CH/^{t}Bu$_2$bpy), 121.6 (C^i/C$_6$H$_3$), 123.6 (C^i/C$_6$H$_3$), 124.2 (CH/^{t}Bu$_2$bpy), 128.4 (C^i/C$_6$H$_3$), 131.0 (CH/C$_6$H$_3$), 134.5 (CH/C$_6$H$_3$), 134.8 (CH/C$_6$H$_3$), 152.9 (CH/^{t}Bu$_2$bpy), 155.8 (C^i/^{t}Bu$_2$bpy), 162.9 (C^i/^{t}Bu$_2$bpy), 193.0 (CO), 198.3 (CO).

9: Anal. Calcd for C$_{64}$H$_{60}$FeN$_4$O$_6$Re$_2$×1/2C$_7$H$_8$ (1455.51): C, 55.70; H, 4.43; N, 3.85. Found: C, 56.03; H, 4.31; N, 3.61. Mp: >215 °C (dec). IR (KBr, cm^{-1}): 1898, 2004 (s, ν_{CO}), 2089 (w, $\nu_{C\equiv CRe}$), 2213 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, CDCl$_3$): 1.46 (s, 36 H, ^{t}Bu), 4.13 (s, 5 H, C$_5$H$_5$), 4.15 (pt, J_{HH} = 1.9 Hz, 2 H, H^β/C$_5$H$_4$), 4.32 (pt, J_{HH} = 1.9 Hz, 2 H, H^α/C$_5$H$_4$), 6.41 (t, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 6.58 (d, J_{HH} = 1.6 Hz, 2 H, C$_6$H$_3$), 7.42 (dd, J_{H5H6} = 6.0 Hz, J_{H5H3} = 1.9 Hz, 4 H, $H3$/^{t}Bu$_2$bpy), 8.07 (d, J_{H3H5} = 1.9 Hz, 4 H, $H3$/^{t}Bu$_2$bpy), 8.90 (d, J_{H6H5} = 6.0 Hz, 4 H, $H6$/^{t}Bu$_2$bpy). MS (ESI-TOF, m/z): 1409.7 [M + H]$^+$, 539.3 [(^{t}Bu$_2$bpy)(CO)$_3$Re]$^+$.

Preparation of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$RuC≡C]C$_6$H$_3$ (12). To 85 mg (0.098 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(HC≡C)C$_6$H$_3$ (**8**) and 65 mg (0.090 mmol) of [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$RuCl] (**10**) dissolved in a mixture of dichloromethane/methanol (40 mL, ratio 1:1) were simultaneously added 18 mg (0.110 mmol) of [NH$_4$]PF$_6$ and 14 mg (0.125 mmol) of KO^{t}Bu. The resulting reaction mixture was stirred for 5 h at 25 °C. The complete conversion of [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$RuCl] (**10**) was monitored by ^{31}P{^{1}H} NMR spectroscopy. Subsequently, all volatiles were removed in an oil-pump vacuum, and the residue was purified by column chromatography on silica gel. The excess of **8** was eluted as an orange band using toluene/dichloromethane (5:1, v/v) as eluent. The title compound was eluted with a mixture of toluene/tetrahydrofuran (10:1, v/v), giving after removal of the solvents in vacuum an orange-red solid. Yield: 88 mg (0.056 mmol, 63% based on **8**).

Anal. Calcd for C$_{84}$H$_{71}$FeN$_2$O$_3$P$_2$ReRu (1561.57): C, 64.61; H, 4.58; N, 1.79. Found: C, 65.09; H, 5.03; N, 1.62. Mp: >175 °C (dec). IR (KBr, cm^{-1}): 1901, 2003 (s, ν_{CO}), 2064 (m, $\nu_{C\equiv CRu}$), 2096 (w, $\nu_{C\equiv CRe}$), 2220 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, CDCl$_3$): 1.45 (s, 18 H, ^{t}Bu), 4.19 (pt, J_{HH} = 1.9 Hz, 2 H, H^β/C$_5$H$_4$), 4.21 (s, 5 H, C$_5$H$_5$/Fc), 4.26 (s, 5 H, C$_5$H$_5$/Ru), 4.42 (pt, J_{HH} = 1.9 Hz, 2 H, H^α/C$_5$H$_4$), 6.57 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 6.82 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 6.97 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.03−7.23 (m, 18 H, C$_6$H$_5$), 7.39−7.48 (m, 12 H, C$_6$H$_5$ + 2 H ($H5$/^{t}Bu$_2$bpy)), 8.09 (d, $^4J_{H3H5}$ = 1.7 Hz, 2 H, $H3$/^{t}Bu$_2$bpy), 9.01 (d, J_{H6H5} = 5.8 Hz, 2 H, $H6$/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 49.4 (s, RuPPh$_3$). MS (ESI-TOF, m/z): 1563.1 [M + H]$^+$, 719.0 [(PPh$_3$)$_2$(C$_5$H$_5$)Ru(CO)]$^+$.

Preparation of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[(η^5-C$_5$H$_5$)(Ph$_3$P)$_2$OsC≡C]C$_6$H$_3$ (13). A mixture of 70 mg (0.081 mmol) of [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$OsBr] (**11**), 80 mg (0.092 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(HC≡C)C$_6$H$_3$ (**8**), and 15 mg (0.092 mmol) of [NH$_4$]PF$_6$ was stirred in methanol (50 mL) for 3 h at reflux, whereby the orange suspension turned into a clear red solution. The reaction mixture was allowed to cool to room temperature, and then sodium metal (5 mg) was added with stirring, causing the precipitation of a yellow solid. All volatile materials were removed under reduced pressure, and the residue was subjected to column chromatography on silica gel. By using first toluene/dichloromethane (5:1, v/v) as eluent, the excess of **8** was removed. Changing the eluent to toluene/tetrahydrofuran (10:1, v/v), afforded,

after removal of all volatiles, the title complex **13**. Yield: 90 mg (0.055 mmol, 67% based on **11**).

Anal. Calcd for C$_{84}$H$_{71}$FeN$_2$O$_3$OsP$_2$Re (1650.73): C, 61.12; H, 4.34; N, 1.70. Found: C, 61.42; H, 4.47; N, 1.75. Mp: >178 °C (dec). IR (KBr, cm^{-1}): 1893, 2003 (s, ν_{CO}), 2065 (m, $\nu_{C\equiv COs}$), 2212 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, CDCl$_3$): 1.45 (s, 18 H, ^{t}Bu), 4.19 (pt, J_{HH} = 1.8 Hz, 2 H, H^β/C$_5$H$_4$), 4.21 (s, 5 H, C$_5$H$_5$/Fc), 4.34 (s, 5 H, C$_5$H$_5$/Os), 4.42 (pt, J_{HH} = 1.8 Hz, 2 H, H^α/C$_5$H$_4$), 6.54 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 6.80 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 6.93 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.03−7.23 (m, 18 H, C$_6$H$_5$), 7.39−7.48 (m, 12 H, C$_6$H$_5$), 7.45 (dd, $^3J_{H5H6}$ = 5.8 Hz, $^4J_{H5H3}$ = 2 Hz, 2 H, $H5$/^{t}Bu$_2$bpy), 8.08 (d, $^4J_{H3H5}$ = 2 Hz, 2 H, $H3$/^{t}Bu$_2$bpy), 9.01 (d, $^3J_{H6H5}$ = 5.8 Hz, 2 H, $H6$/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 0.6 (s, OsPPh$_3$). MS (ESI-TOF, m/z): 1651.2 [M + H]$^+$, 539.1 [(^{t}Bu$_2$bpy)(CO)$_3$Re]$^+$, 809.1 [(PPh$_3$)$_2$(C$_5$H$_5$)Os(CO)]$^+$.

Preparation of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(PPh$_3$)$_2$(Cl)PtC≡C]C$_6$H$_3$ (15). To 100 mg (0.115 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(HC≡C)C$_6$H$_3$ (**8**) and 135 mg (0.171 mmol) of *cis*-[(PPh$_3$)$_2$PtCl$_2$] (**14**) dissolved in 15 mL of chloroform was added 0.5 mL of diethylamine. The resulting reaction mixture was stirred for 5 h at reflux. After cooling to room temperature all volatiles were removed in an oil-pump vacuum, and the residue was purified by column chromatography on silica gel using a mixture of dichloromethane/toluene (2:1, v/v) as eluent. Complex **15** was obtained as an orange powder. Yield: 110 mg (0.068 mmol, 59% based on **8**).

Anal. Calcd for C$_{79}$H$_{66}$ClFeN$_2$O$_3$P$_2$PtRe (1625.93): C, 58.36; H, 4.09; N, 1.72. Found: C, 58.31; H, 4.02; N, 1.25. Mp: >178 °C (dec). IR (KBr, cm^{-1}): 1898, 2004 (s, ν_{CO}), 2090 (m, $\nu_{C\equiv CRe}$), 2116 (w, $\nu_{C\equiv CPt}$), 2211 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, CDCl$_3$): 1.43 (s, 18 H, ^{t}Bu), 4.17 (s, 5 H, C$_5$H$_5$), 4.18 (pt, J_{HH} = 1.9 Hz, 2 H, H^β/C$_5$H$_4$), 4.36 (pt, J_{HH} = 1.9 Hz, 2 H, H^α/C$_5$H$_4$), 5.77 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 5.80 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 6.49 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.31−7.46 (m, 20 H (C$_6$H$_5$) + 2 H ($H5$/^{t}Bu$_2$bpy)), 7.67−7.80 (m, 10 H, C$_6$H$_5$), 8.05 (d, $^4J_{H3H5}$ = 1.7 Hz, 2 H, $H3$/^{t}Bu$_2$bpy), 8.96 (d, $^3J_{H6H5}$ = 5.8 Hz, 2 H, $H6$/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 20.5 ($^1J_{31P195Pt}$ = 2656.7 Hz, PtPPh$_3$). MS (ESI-TOF, m/z): 1626.8 [M + H]$^+$, 539.3 [(^{t}Bu$_2$bpy)(CO)$_3$Re]$^+$.

Preparation of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC'C]-5-(Br-4-C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-3,5-C≡C-1)C$_6$H$_3$ (17). To a mixture of 150 mg (0.172 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(HC≡C)C$_6$H$_3$ (**8**) and 65 mg (0.165 mmol) of Br-1-I-4-C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6 (**16**) in 10 mL of tetrahydrofuran and 15 mL of diisopropylamine were added [(PPh$_3$)$_2$PdCl$_2$] (55 mg) and [CuI] (25 mg). The reaction mixture was stirred for 2 h at 35 °C. Afterward, all volatiles were removed under reduced pressure and the remaining residue was purified by column chromatography on silica gel using a mixture of petroleum ether/tetrahydrofuran (10:1, v/v) as eluent. Compound **17** was further purified by precipitation from a concentrated dichloromethane solution (2 mL) with *n*-hexane (20 mL) and washed twice with 10 mL portions of *n*-hexane. After drying in an oil-pump vacuum compound **17** was obtained as an orange solid. Yield: 135 mg (0.118 mmol, 68% based on **16**).

Anal. Calcd for C$_{55}$H$_{54}$BrFeN$_4$O$_3$Re×1/2CH$_2$Cl$_2$ (1183.46): C, 56.33; H, 4.68; N, 4.73. Found: C, 56.52; H, 4.85; N, 4.65. Mp: >172 °C (dec). IR (KBr, cm^{-1}): 1901, 2004 (s, ν_{CO}), 2090 (w, $\nu_{C\equiv CRe}$), 2215 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, CDCl$_3$): 1.47 (s, 18 H, ^{t}Bu), 2.32 (s, 12 H, NMe$_2$), 3.52 (s, 4 H, CH$_2$), 4.20 (s, 5 H, C$_5$H$_5$), 4.21 (pt, J_{HH} = 1.9 Hz, 2 H, H^β/C$_5$H$_4$), 4.42 (pt, J_{HH} = 1.9 Hz, 2 H, H^α/C$_5$H$_4$), 7.00 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.05 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.24 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$H$_3$), 7.43 (s, 2 H, C$_6$H$_2$), 7.48 (dd, $^3J_{H5H6}$ = 5.8 Hz, $^4J_{H5H3}$ = 1.9 Hz, 2 H, $H5$/^{t}Bu$_2$bpy), 8.10 (d, $^4J_{H3H5}$ = 1.9 Hz, 2 H, $H3$/^{t}Bu$_2$bpy), 8.99 (d, $^3J_{H6H5}$ = 5.8 Hz, 2 H, $H6$/^{t}Bu$_2$bpy). MS (ESI-TOF, m/z): 1141.4 [M + H]$^+$, 539.2 [(^{t}Bu$_2$bpy)(CO)$_3$Re]$^+$.

Preparation of {1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(C≡C)C$_6$H$_3$}$_2$ (18). To a pyridine solution (10 mL) containing

[CuCl] (3 mg, 0.031 mmol) was added a solution of 100 mg (0.115 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(HC≡C)C$_6$H$_3$ (**8**) in dry pyridine (10 mL), and the mixture was stirred for 1 h under an oxygen atmosphere at 40 °C. Afterward all volatiles were removed under reduced pressure, giving a residual solid that was subjected to column chromatography on silica gel using diethyl ether/*n*-hexane (3:1, v/v) as eluent. The product was further purified by precipitation from a concentrated dichloromethane solution (2 mL) with *n*-hexane (20 mL) and washed twice with 10 mL portions of *n*-hexane. After drying in an oil-pump vacuum compound **18** was obtained as an orange solid. Yield: 90 mg (0.052 mmol, 90%).

Anal. Calcd for C$_{86}$H$_{72}$Fe$_2$N$_4$O$_6$Re$_2$×1/2CH$_2$Cl$_2$ (1784.09): C, 58.23; H, 4.12; N, 3.14. Found: C, 58.15; H, 4.01; N, 2.92. Mp: >190 °C (dec). IR (KBr, cm^{-1}): 1901, 2005 (s, ν_{CO}), 2088 (w, $\nu_{C≡CRe}$), 2213 (w, $\nu_{C≡CFc}$). ^{1}H NMR (δ, CDCl$_3$): 1.48 (s, 36 H, ^{t}Bu), 4.20 (s, 10 H, C$_5$*H*$_5$), 4.22 (pt, J_{HH} = 1.9 Hz, 4 H, *H*$^{\beta}$/C$_5$H$_4$), 4.43 (pt, J_{HH} = 1.9 Hz, 4 H, *H*$^{\alpha}$/C$_5$H$_4$), 6.93 (pt, J_{HH} = 1.6 Hz, 2 H, C$_6$*H*$_3$), 7.11 (pt, J_{HH} = 1.6 Hz, 2 H, C$_6$*H*$_3$), 7.21 (pt, J_{HH} = 1.6 Hz, 2 H, C$_6$*H*$_3$), 7.49 (dd, $^3J_{H5H6}$ = 5.8 Hz, $^4J_{H5H3}$ = 2 Hz, 4 H, *H5*/^{t}Bu$_2$bpy), 8.10 (d, $^4J_{H3H5}$ = 2 Hz, 4 H, *H3*/^{t}Bu$_2$bpy), 8,98 (d, $^3J_{H5H6}$ = 5.8 Hz, 4 H, *H6*/^{t}Bu$_2$bpy).

Crystal Structure Determinations. Crystal data for **6**, **8**, **12**, **13**, and **15** are presented in Table 5. The data for **6** were collected on a Bruker Smart CCD 1k diffractometer and for **8**, **12**, **13**, and **15** on a Oxford Gemini S diffractometer with graphite-monochro-matized Mo Kα radiation (λ = 0.71073 Å) at 293(2) K using oil-coated shock-cooled crystals.[51] The structures were solved by direct methods using SHELXS-97[52] or SIR-92[53] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[54] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions.

Supporting Information Available: Tables of atomic coordinates, bond lengths, angles, torsion angles, and anisotropic displacement parameters for **6**, **8**, **12**, **13**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800206K

(51) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615. (b) Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465. (c) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.
(52) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(53) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gualardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(54) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen, 1997.