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Bis(cyclopentadienyl)phenylphosphine as Ligand Precursor for Assembling Heteropolymetal Complexes

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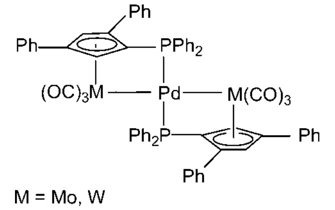
The dilithium salt of bis(cyclopentadienyl)phenylphosphine has been used as a multidentate ligand to generate unprecedented heteropolymetal arrays via the bimetal precursors $[MI(CO)_3]_2[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)]$ (**9**, M = Mo; **10**, M = W). The trimetal complexes $MI(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MPd(PPh_3)I$ (**14**, M = Mo; **15**, M = W), obtained by reaction of **9** and **10** with $Pd(PPh_3)_4$, respectively, have been found to lose PPh_3 converting to the hexametal derivatives $\{MI(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MPd\}(\mu\text{-}I_2)\{PdM(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MI\}$ (**18**, M = Mo; **19**, M = W). Compound **18** also has been prepared by reaction of **9** with a PPh_3-free zerovalent palladium species such as $Pd_2(dba)_3$; treatment of **18** with PPh_3 regenerated the trimetal complex **14**. The pentametal complex $\{MoI(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3Mo\}Pd\{Mo(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MoI\}$ (**22**), containing a linear Mo−Pd−Mo array, has been spectroscopically observed by reacting **18** with 1,2-bis(diphenylphosphino)ethane.

Introduction

As part of our studies of Pd-assisted metal–carbon and metal−metal bond-forming reactions,[1,2] we have recently communicated the synthesis and characterization of trimetal complexes containing linear M−Pd−M arrays (M = Mo, W)[2d] (Chart 1).

Since early late heteropolymetal complexes have relevance to catalysis[3] as well as to the construction of metal-containing oligomers and polymers,[4] a project has been initiated aimed at rationalizing the design of heteropolymetal compounds containing M−Pd and M−Pd−M moieties where M is an early transition metal. To this purpose, our attention was immediately attracted by bis(cyclopentadienyl)phenylphosphine (bcp) that, upon simple lithiation, affords a tridentate ligand (Li_2bcp) with a great potential to assemble homo- and heteropolymetal structures.[5–9] Previous examples of metal complexes stabilized by bcp^{2-} are shown in Chart 2. These include structures of type

Chart 1



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† ICCOM-CNR, Florence, Italy.

(1) (a) Lo Sterzo, C. *Synlett* **1999**, 1704. (b) Antonelli, E.; Rosi, P.; Lo Sterzo, C.; Viola, E. *J. Organomet. Chem.* **1999**, *578*, 210. (c) Altamura, P.; Giardina, G.; Lo Sterzo, C.; Russo, M. V. *Organometallics* **2001**, *20*, 4360. (d) La Groia, A.; Ricci, A.; Bassetti, M.; Masi, D.; Bianchini, C.; Lo Sterzo, C. *J. Organomet. Chem.* **2003**, *683*, 406.

(2) (a) Tollis, S.; Narducci, V.; Cianfriglia, P.; Lo Sterzo, C.; Viola, E. *Organometallics* **1998**, *17*, 2388. (b) Ricci, A.; Angelucci, F.; Bassetti, M.; Lo Sterzo, C. *J. Am. Chem. Soc.* **2002**, *124*, 1060. (c) Ricci, A.; Lo Sterzo, C. *J. Organomet. Chem.* **2002**, *653*, 177. (d) Angelucci, F.; Ricci, A.; Lo Sterzo, C.; Masi, D.; Bianchini, C.; Bocelli, G. *Organometallics* **2002**, *21*, 3001. (e) Angelucci, F.; Ricci, A.; Masi, D.; Bianchini, C.; Lo Sterzo, C. *Organometallics* **2004**, *23*, 4105.

(3) (a) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109. (b) Bianchini, C.; Meli, A.; Vizza, F. *Eur. J. Inorg. Chem.* **2001**, *43*, 43. (c) Wheatley, N.; Kalck, P. *Chem. Rev.* **1999**, *99*, 3379. (d) Makoto, M.; Shinichi, K.; Norio, K.; Terunori, F. *Curr. Trends Polym. Sci.* **2001**, *6*, 85.

(4) (a) Fujimura, T.; Seino, H.; Hidai, M.; Mizobe, Y. *J. Organomet. Chem.* **2004**, *689*, 738 and references cited therein. (b) Zhang, K.; Chen, Z.; Zou, Y.; Yang, C.; Qin, J.; Cao, Y. *Organometallics* **2007**, *26*, 3699.

(5) For different use of cyclopentadienyls and other aromatic units containg either alkylene or alkenylene spacers and a variety of heteroatom-centered groups based on B, Ge, Si, Sn, P, As, and S, see also: (a) Lee, I.; Dahan, F.; Maisonnat, A.; Poilblanc, R. *Organometallics* **1994**, *13*, 2743. (b) Viotte, M.; Gautheron, B.; Kubicki, M.; Mugnier, Y.; Parish, R. V. *Inorg. Chem.* **1995**, *34*, 3465. (c) Curnow, O. J.; Huttner, G.; Smail, S. J.; Turnbull, M. M. *J. Organomet. Chem.* **1996**, *524*, 267. (d) Iretskii, A.; Jennings, M. C.; Poilblanc, R. *Inorg. Chem.* **1996**, *35*, 1266. (e) Schaverien, C. J.; Ernst, R.; Terlouw, W.; Schut, P.; Sudneijer, O.; Budzelaar, P. H. M. *J. Mol. Catal. A: Chem.* **1998**, *128*, 245. (f) Shin, J. H.; Hascall, T.; Parkin, G. *Organometallics* **1999**, *18*, 6. (g) Shapiro, P. *Coord. Chem. Rev.* **2002**, *231*, 67. (h) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525. (i) Erker, G.; Kehr, G.; Fröhlich, R. *J. Organomet. Chem.* **2004**, *689*, 1402.

(6) (a) Köpf, H.; Khal, W. *J. Organomet. Chem.* **1974**, *64*, C37. (b) Köpf, H.; Klouras, N. *Monatsh. Chem.* **1983**, *114*, 243.

(7) Troitskaya, L. L.; Ovseenko, S. T.; Krylova, A. I.; Sokolov, V. I. *Russ. Chem. Bull.* **2001**, *50* (11), 2212.

(8) (a) Mathey, F.; Lampin, J. P. *J. Organomet. Chem.* **1977**, *128*, 297. (b) Herberhold, M.; Biersack, M. J. *Organomet. Chem.* **1990**, *381*, 379. (c) Imamura, Y.; Kubo, K.; Mizuta, T.; Miyoshi, K. *Organometallics* **2006**, *25*, 2301.

10.1021/om701221p CCC: $40.75

Chart 2

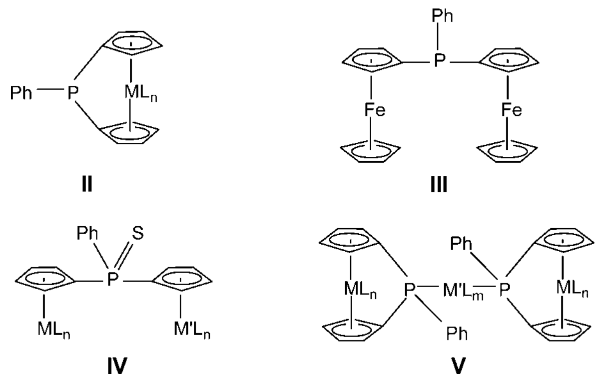
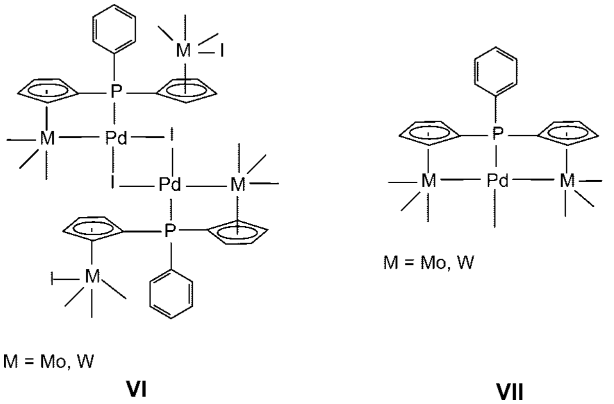


Chart 3



II,[6] where both Cp units are bound to the same metal center such as in “molecular tweezers”, structures of type **III**,[7] where each Cp unit is part of an independent ferrocenyl fragment, structures of type **IV**, where each Cp unit holds in a half-sandwich fashion two different metal centers,[8] or structures of type **V**, where bcp^{2-} uses all its donor atoms to form a trimetal species.[9]

In this paper, we describe our approach to the design of unprecedented hexametallic structures of type **VI** (Chart 3), where two halo-bridged palladium centers are bonded to an early transition metal from a half-sandwich metallocene. The molecular structure is completed by two half-metallocenes exhibiting no bonding interaction with the Pd centers.

Spectroscopic evidence for the formation of polymetal structures of type **VII** (Chart 3), containing linear M−Pd−M arrays with metal−metal bond interactions, is also reported. Due to the half-sandwich coordination of the early transition metals and the vacant site at Pd,[10] structures of the latter type are promising building blocks for creating new heteropolymetal assemblies.

Results and Discussion

Preparation of [MI(CO)$_3$]$_2$[(η^5-C$_5$H$_4$)P(Ph)(η^5-C$_5$H$_4$)] (M = Mo, 9; M = W, 10). The homobimetal complexes **9** and **10** were prepared as described in Scheme 1. While CpTl (**1**) was purchased from a commercial supplier, bis(cyclopentadienyl)phenylphosphine **3** was synthesized by modifying a procedure previously reported by Lampin.[6b,11] The complete conversion of dichlorophenylphosphine **2** into **3** was achieved by using a 4-fold excess of **1**[12] that was later eliminated from the reaction mixture by using Et$_2$O as reaction solvent. In this solvent, both **1** and the byproduct TlCl are scarcely soluble, in fact, so that they could be separated from **3** by simple filtration. After solvent evaporation, **3** was used in the next reaction step with no need of further purification. Crude **3** was actually dissolved in THF to give a solution that, upon treatment with 2 equiv of BuLi at 0 °C, contained exclusively the bis(cyclopentadienyl) dianion **4**. To the solution of this dilithium salt was added with stirring M(CH$_3$CN)$_3$(CO)$_3$ (M = Mo, **5**; M = W, **6**) and the resulting reaction mixture was first stirred overnight at room temperature, then refluxed for 2 h. Finally, the addition of stoichiometric 1,2-diiodoethane led to the formation of **9** and **10**, likely through intermediates **7** and **8**, respectively. All our attempts to isolate **9** and **10** in the pure form by chromatographic techniques were unsuccessful due to extensive on-column decomposition.[13] However, when the crude mixture containing **9** or **10** was filtered through a Celite pad and the solvent was evaporated to small volume, then the simple addition of *n*-pentane caused the precipitation of pure **9** and **10** as dark red microcrystals, which were isolated in 63% and 68% yield, respectively.

Compounds **9** and **10** have been unambiguously characterized by IR, MS, and multinuclear NMR spectroscopy. The solid-state molecular structure of **9** has been determined by an X-ray diffraction analysis of a single crystal obtained by liquid diffusion recrystallization of the crude product with dichloromethane/*n*-pentane (Figure 1). Crystal and structural refinement data for **9** are listed in Table 1.

In the molecular structure of **9**, the two Mo(CO)$_3$I groups are pseudo-trans to each other, very likely for steric reasons, so as to give a locked system with no possibility to exchange their position also in solution (vide infra). For this reason, **9** should exist as an atropoisomeric mixture of the two isomers **9a** and **9b** (Figure 1). The crystal studied by X-ray diffraction analysis was stereoisomer **9a**, featured by a torsion angle of 54.3° between the planes of the two Cp rings. Because of the rigid *transoid* configuration of the two Mo(CO)$_3$I units, one Mo(CO)$_3$I group is facing the phosphorus lone pair in one side of the ligand plane, while the second Mo(CO)$_3$I fragment is facing the phenyl unit on the opposite face.

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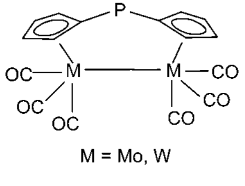
[9] Anderson, G. K.; Lin, M. *Inorg. Chim. Acta* **1988**, *142*, 7.

[10] (a) Braunschweig, H.; Breitling, F. M.; Burschka, C.; Seeler, F. *J. Organomet. Chem.* **2006**, *691*, 702. (b) Morandini, F.; Munari, I.; Panese, M.; Ravazzolo, A.; Consiglio, G. *Inorg. Chim. Acta* **2005**, *358*, 2697.

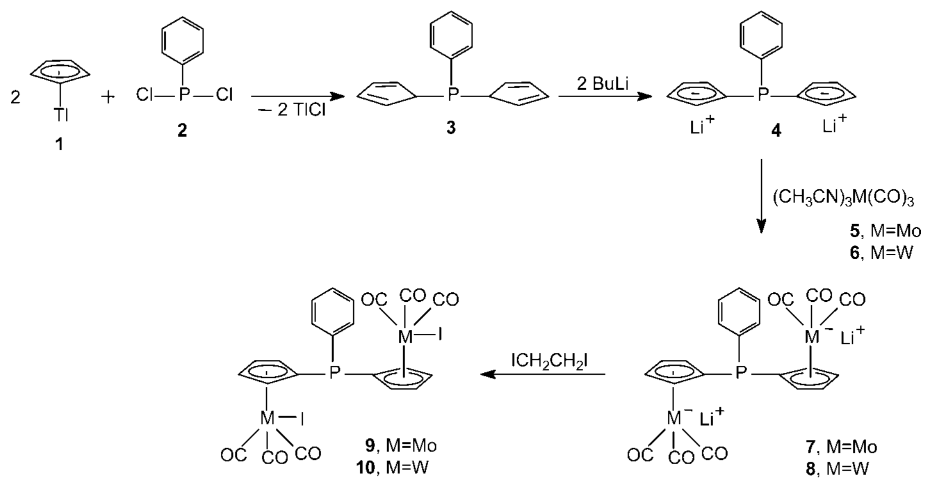
[11] Mathey, F.; Lampin, J. P. *Tetrahedron* **1975**, *31*, 2685.

[12] The reaction of **1** and **2** in the 2/1 stoichiometric ratio always affords the *mono*substituted derivative Cl−P(Ph)−(C$_5$H$_4$) (Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1987**, *6*, 872) as the main product.

[13] Although ^{31}P NMR analysis of a sample of crude reaction mixture clearly indicated the complete and exclusive formation of **9** and **10**, the subsequent chromatographic purification always produced three different products. The first eluted band (deep red) gave, after solvent evaporation, a small amount of a dark solid whose characterization is still under investigation. The second eluted fraction (red) was identified as the expected product, and the third (purple) fraction after evaporation of the solvent gave a red-purple solid that was identified by NMR spectroscopy and mass spectroscopy as the dimeric complex (Shin, J. H.; Parkin, G. *Inorg. Chem. Commun.* **1999**, *2*, 428) represented in the following structure.



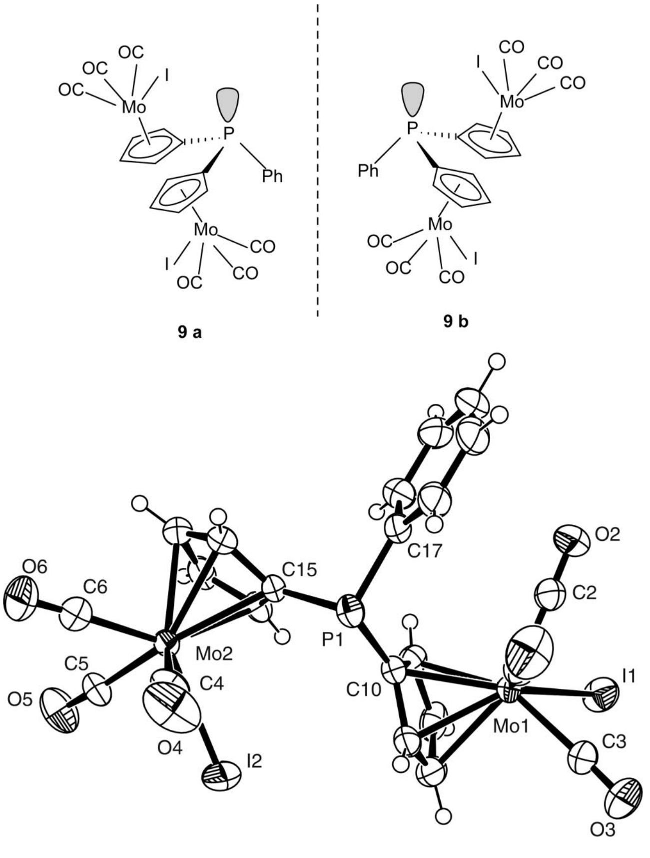
Scheme 1



The rigid *transoid* disposition of the $M(CO)_3I$ moieties (M = Mo (**9**), W (**10**)), with respect to the bis(cyclopentadienyl)phenylphosphine ligand, is likely maintained also in solution as shown by the ^1H and ^{13}C NMR spectra displaying four distinct resonances for the Cp protons and five distinct resonances for the Cp carbons, respectively.[14]

Selected bond distances and angles are given in Table 2 (see the Supporting Information for full listings) The Cp_1−P−Ph and Cp_2−P−Ph angles measure 98.0° and 104.6°, respectively, which reflects the distortion of the system caused by the opposite orientation of the $Mo(CO)_3I$ units. In this way, the Cp_2 ring can adopt a spatial conformation that minimizes the contact between the phenyl and the $Mo(CO)_3I$ fragment forcing, on the other hand, an ortho hydrogen atom of the phenyl group to assume a position close to that of the C(1) atom of the Cp_1 ring (2.778 Å). Interestingly, one of the coordinated iodine atoms, as already established in a similar compound,[15] lies in close proximity to the phosphorus atom, with no covalent bonding interaction as shown by the interatomic distance (4.288 Å), which exceeds the sum of the van der Waals radii.[16]

The bis(cyclopentadienyl)phenylphosphine ligand adopts the 1,1′-(η^5:η^5) binding mode, and the Mo centers have a four-legged piano stool structure (square pyramidal). In **9**, the C−P



9 a **9 b**

Figure 1. Atropoisomers **9a** and **9b** and ORTEP drawings of compound **9**.

Table 1. Crystal Data and Structure Refinement Details for 9

empirical formula	$C_{22}H_{13}I_2Mo_2O_6P_5$
fw	849.97
temp [K]	293(2)
wavelenght [Å]	0.71069
cryst system, space group	monoclinic
a [Å]	11.859(3)
b [Å]	18.165(5)
c [Å]	12.637(4)
α [deg]	90
β [deg]	111.89(2)
γ [deg]	90
V [Å^3]	2526.0(12)
Z, D_c [g cm^{-3}]	4, 2.235
abs coeff [mm^{-1}]	3.535
F(000)	1592
cryst size [mm^3]	0.375 × 0.125 × 0.075
Θ range for data collection [deg]	2.01–24.98
limiting indices	$-14 \le h \le =13$
	$0 \le k \le 21$
	$0 \le l \le 15$
no. of reflns collected/unique	4640/4429
GOF on F^2	1.020
no. of data/restraints/parameters	4429/0/287
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0315, *w*R2 = 0.0675
R indices (all data)	R1 = 0.0599, *w*R2 = 0.0756
largest diff peak and hole [e Å^{-3}]	0.838 and −0.987

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 9

Mo(1)−I(1)	2.8406(9)
Mo(2)−I(2)	2.8308(9)
P(1)−C(10)	1.829(5)
P(1)−C(15)	1.840(5)
C(10)−P(1)−C(17)	104.6(2)
C(17)−P(1)−C(15)	98.07(19)

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[14] Ebels, J.; Pietschnig, R.; Kotila, S.; Dombrowski, A.; Niecke, E.; Nieger, M.; Schiffner, H. M. *Eur. J. Inorg. Chem.* **1998**, 331.

[15] Brownie, J. H.; Baird, M. C.; Schmider, H. *Organometallics* **2007**, *26*, 1433.

[16] Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, U.K., 1991.

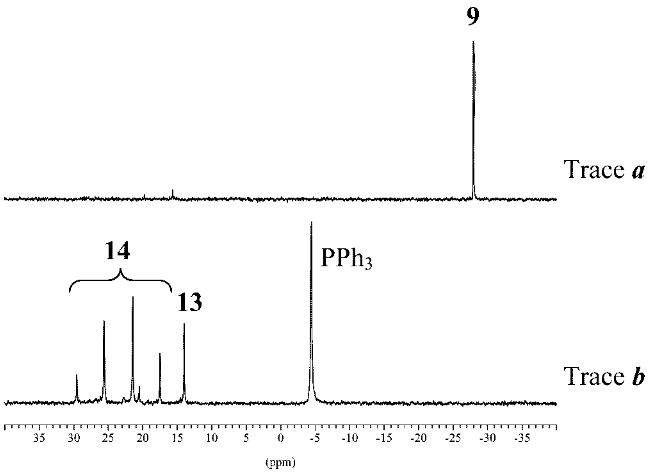

Figure 2. In situ $^{31}P\{^1H\}$ NMR study in $CDCl_3$ of the reaction between **9** and $Pd(PPh_3)_4$.

distances P(1)−C(10) and P(1)−C(15), respectively, and the C═O bond lengths (from (1.118(6) Å to (1.140(7) Å) are within the expected range.[17] The Mo−Cp ring carbon distances range from 2.270(5) to 2.381(5) Å, consistent with Mo−Cp ring carbon distances expected for other compounds.[15] The Mo−I distances, Mo(1)−I(1) 2.8406(9) Å and Mo(2)−I(2) 2.8308(9) Å, also fall in the normal range of distances.[17]

Reactions of 9 and 10 with $Pd(PPh_3)_4$ and $Pd_2(dba)_3$. The reactions of **9** and **10** with $Pd(PPh_3)_4$ were preliminarily carried out in NMR tubes and were followed by $^{31}P\{^1H\}$ NMR spectroscopy.

In trace a of Figure 2 is reported the spectrum of **9** in $CDCl_3$ (singlet at −30.1 ppm). Upon addition of 2 equiv of $Pd(PPh_3)_4$, all **9** disappeared with formation of three products: free PPh_3, the square-planar trans-complex $Pd(I)_2(PPh_3)_2$[18,19] (**13**) at 13.5 ppm, and a major compound featured by an AB spin system centered at 21.5 ppm with $J_{PP} = 491$ Hz (simulated value),[20] hence attributable to the trans phosphorus atoms.[21]

Of the two possible structures that one may propose for the product featured by the AB pattern (Scheme 2), the structure containing a trimetallic Mo−Pd−Mo array (**11**) was initially taken as the more likely just in view of the formation of byproduct **13**.[22] This interpretation was later discarded on the basis of experimental evidence pointing to $MoI(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MoPd(PPh_3)I$ (**14**) as the product with the *trans*-P atoms (vide infra).

All our attempts to isolate **14** in the pure form from the reaction mixture by chromatographic techniques were unsuccessful, a unique fraction containing **14**, **13**, and a third complex featured by two singlets at 37.7 and 37.3 ppm being invariably obtained (Figure 3, trace a). The persistent appearance of the latter two compounds, even after repeated chromatographic purifications, led us to consider the occurrence of a transformation of **14** under chromatographic conditions. This hypothesis was confirmed by the fact that the addition of an excess of PPh_3 to the mixture resulted in the disappearance of the peaks at 37.7 and 37.3 ppm and the selective formation of **14** (Figure 3, trace b). Apparently, under chromatographic conditions, **14** releases PPh_3 to give a species that regenerates **14** upon PPh_3 uptake. It has been ascertained (vide infra) that this new species is the $\mu\text{-}(I)_2$ dimer $\{MoI(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MoPd\}(\mu\text{-}I_2)\{PdMo(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MoI\}$ (**18**), which exists as two diastereoisomers (Scheme 2).

It is noteworthy that the mechanism of formation of **18** as well as its structure have a close precedent in the conversion of compound **20** into **21**, recently reported by some of us (Scheme 3).[2b,e]

Further conclusive evidence of the formation of the dimer **18** as well as of the reversible release/uptake of PPh_3 by **14**/**18** was provided by an in situ NMR experiment (Scheme 4). Complex **9** was dissolved in $CDCl_3$ and a $^{31}P\{^1H\}$ NMR spectrum (singlet at −30.1 ppm) was acquired at room temperature (Figure 4 trace a). To this solution was added 1 equiv of $Pd_2(dba)_3$, which caused the immediate and complete conversion of **9** into **18** (Figure 4, trace b). Finally, the addition of 1 equiv of PPh_3 regenerated the characteristic AB system of **14** together with the singlet at 13.5 ppm due to **13**.

As previously anticipated, the dimer **18** is actually a mixture of two diastereomers, *rac dl*-**18a** and *meso*-**18b**, due to the stereogenic nature of the two phosphorus atoms (Chart 4), which accounts for the two singlets observed in the $^{31}P\{^1H\}$ NMR spectrum.[23]

The same sequence of reactions and products was obtained with the tungsten precursor **10**.

As regards the mechanism of formation of the square-planar diiodide byproduct **13**, invariably obtained in 15–20% yield from **9** or **10**,[24] no clear-cut explanation can be given at this stage. The most straightforward interpretation is to think of **13** as a thermodynamically stable species resulting from a metathesis reaction between $Pd(PPh_3)_4$ and the M−I moieties in **9** or **10**. In this respect, it is likely that the size and steric properties of PPh_3 may play a crucial role in determining both the *transoid* structure of **14** and **15** as well as the formation of the trans complex **13**. Indeed, as shown by the reaction of **18** with 1,2-diphenylphosphinoethane (dppe) (vide infra), a trimetal linear array actually can be achieved with the bcp^{2-} ligand.[2d]

Formation of Trimetal Linear M−Pd−M Arrays (M = Mo, W). Compound **9** and $Pd_2(dba)_3$ were reacted in a Schlenck flask containing degassed THF. After all **9** was converted to **18** (NMR evidence) (Scheme 5), the solvent was removed under reduce pressure and the residue was redissolved in distilled CH_2Cl_2. Addition of degassed *n*-pentane led to the immediate

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(17) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, *12*, S1–S83.

(18) Amatore, C.; Jutand, A.; Mottier, L. *Eur. J. Inorg. Chem.* **1999**, 1081.

(19) Formation of *trans*-$(PPh_3)_2PdI_2$ (**13**) as side product in the oxidative addition of zerovalent palladium has been reported: Weigelt, M.; Becher, D.; Poetsch, E.; Bruhn, C.; Steinborn, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1542.

(20) The coupling constant for compound **14** was obtained from $^1H\{^{31}P\}$ spectra with the aid of computer simulation, using the *gNMR* program. See: Budzelaar, P. H. M. *gNMR*, V4.0; Cherwell Scientific Publishing, Copyright Iviry soft, 1995–1997.

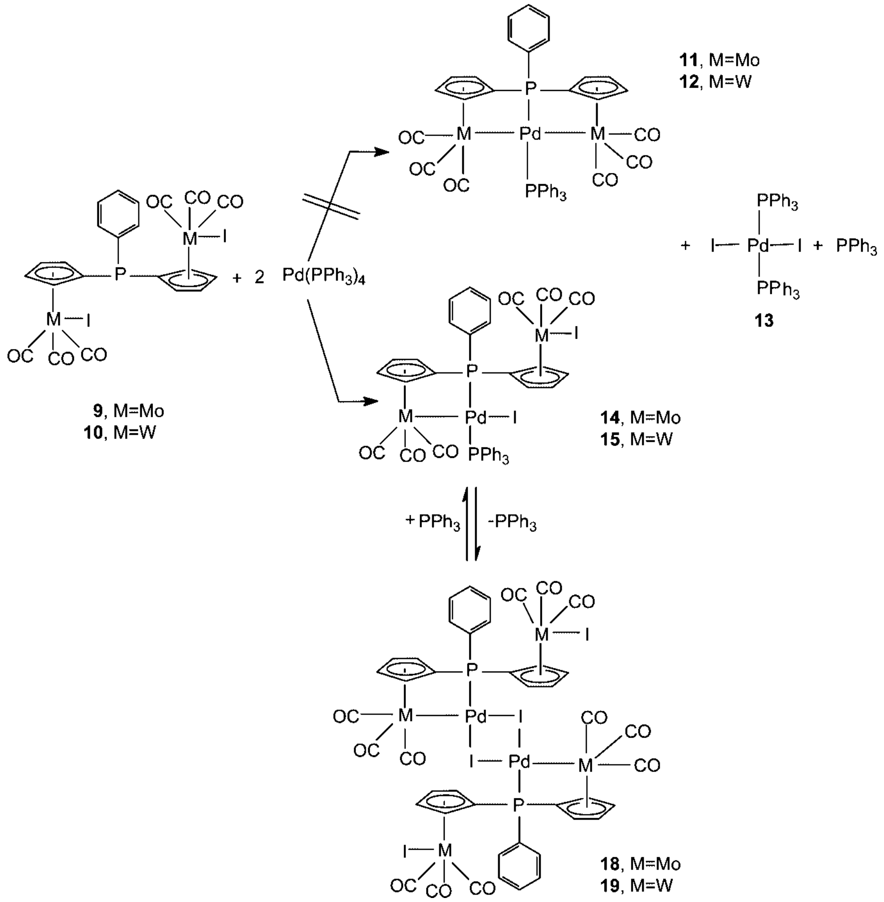
(21) (a) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, *105*, 7574. (b) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

(22) While observation of **13** was retained perfectly coherent with formation of **11** (Scheme 2), its occurrence seemed to rule out formation of **14**. To force formation of **11** we used a twofold excess of $Pd(PPh_3)_4$. One equivalent of Pd would be necessary to form the trimetallic array Mo−Pd−Mo of **11**, while the second equivalent was expected to extract the two iodine groups from **9** with formation of **13**. Moreover, it is worthy of note to underline variations of oxidation numbers of metal centers taking place in the transformations outlined in Scheme 2. Upon formation of **11** and **12** the molybdenum and tungsten atoms of **9** and **10** are reduced from the initial oxidation numbers +2 into +1. Conversely, while the zerovalent palladium entering into **9** and **10** to form **11** and **12** maintains its zero oxidation number, the palladium forming *trans*-$(PPh_3)_2PdI_2$ is oxidized from Pd(0) to Pd(+2).

(23) Haltermann, R. *L. Chem. Rev.* **1992**, *92*, 965.

(24) Formation of compound **13** was also observed upon treatment of dimer **18** with PPh_3 in a 1:2 stoichiometric ratio.

Scheme 2



formation of a dark red precipitate that was isolated by filtration and repeatedly washed with *n*-pentane to eliminate the dba residue. Finally, a chromatographic purification of the crude material over silica gel gave pure **18** as a diastereoisomer mixture (**18a**−**18b**, Chart 4).

Taking into account our recent results obtained for compounds having a dihalide bridged core identical with that shown by **18**,[2d] we focused our attention on the reactivity of the latter compound in the presence of a chelating diphosphine. The reaction of **18** with a stoichiometric amount of dppe (Scheme 5) was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and showed the complete disappearance of **18** and the simultaneous appearance of two new signals at 18.7 and 17.7 ppm, respectively, attributed to the pentametallic compound **22**, flanked by a signal at 62.7 ppm due to the square-planar complex *cis*-(dppe)PdI$_2$ (**23**)[25] (Scheme 5). The signals at 18.7 and 17.7 ppm respectively have been attributed to the formation of the complex **22** according to similar results previously observed by some of us.[2d] This transformation is in line with the observed ability of triphenylphosphine to abstract PdI$_2$ moiety from bcp^{2-} complexes (see Scheme 4).

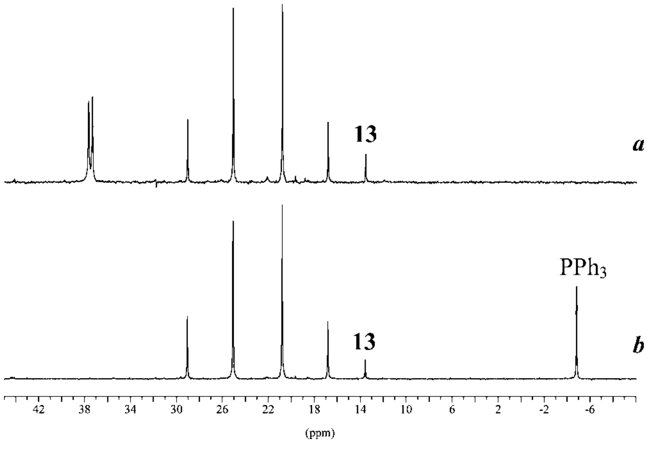
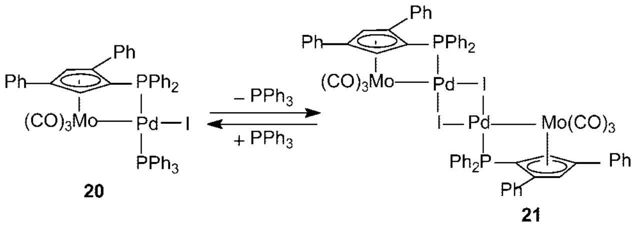


Figure 3. Trace a: $^{31}P\{^1H\}$ NMR spectrum in CDCl$_3$ of the fraction obtained by chromatographic purification of complex **14**. Trace b: $^{31}P\{^1H\}$ NMR spectrum recorded after addition of an excess of PPh$_3$ to the above solution.

Scheme 3



Conclusions

Herein we have shown that the dilithium salt of bis(cyclopentadienyl)phenylphosphine is a versatile $\mu_3[(\eta^5\text{-}Cp):(\eta^5\text{-}Cp'):(\kappa\text{-P})]$ ligand capable of forming polymetal complexes with a variety of structures and stereochemical conformations containing bimetal M−Pd and trimetal M−Pd−M arrays (M = Mo, W). The presence of chemically labile CO−ligands and

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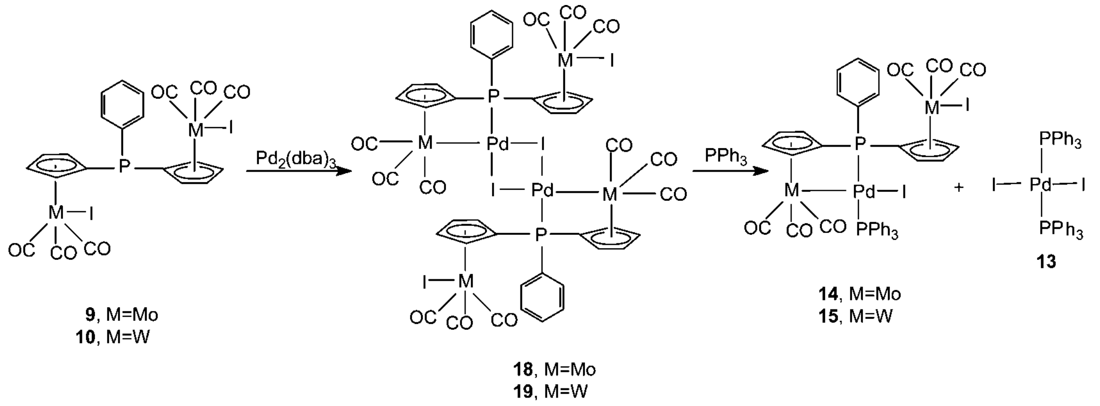
(25) (a) Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50* (5), 1319. (b) Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Brüggeller, P. *Polyhedron* **1997**, *16*, 2827.

Scheme 4



metal−iodide groups at the external Mo or W centers makes the complexes described in this paper potential building blocks to generate more elaborate structures such as multinuclear and/or polymeric inorganic/organometallic materials.[1]

Experimental Section

General Considerations. Elemental analyses were performed with a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of ±0.4 units on carbon (C), hydrogen (H), and nitrogen (N). FT-IR spectra were recorded on a Nicolet 510 instrument in the solvent subtraction mode, using a 0.1 mm CaF$_2$ cell. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on either a Bruker AC300P spectrometer at 300, 75, and 121 MHz, respectively, or Bruker Avance DRX-400 (400.13 and 100.62 MHz, respectively) spectrometers equipped with variable-temperature control units accurate to ±0.1 °C. Chemical shifts are reported in ppm (δ) relative to TMS or referenced to the chemical shifts of residual solvent resonances (^{1}H and ^{13}C). The ^{31}P{^{1}H} NMR chemical shifts are relative to 85% H$_3$PO$_4$. Mass spectra were obtained on a Fisons Instruments VG-Platform Benchtop LC-MS (positive ion electrospray, ESP^{+}) spectrometer. Solvents, including those used for NMR and chromatography, were thoroughly degassed before use. Chromatographic separations were performed with 70–230 mesh silica gel (Merck). All manipulations were carried out with Schlenk-type equipment under an argon atmosphere on a dual manifold/argon-vacuum system. Liquids have been transferred by either syringe or cannula. THF and Et$_2$O were distilled from sodium−potassium alloy. Mo(CH$_3$CN)$_3$(CO)$_3$ and W(CH$_3$CN)$_3$(CO)$_3$ were prepared according to published procedures.[26] (C$_5$H$_5$)Tl, Cl$_2$PPh, BuLi, ICH$_2$CH$_2$I, Pd$_2$(dba)$_3$, and PPh$_3$ were purchased from Aldrich and used as received. Otherwise stated, reagents and solvents have been used as received from the commercial suppliers.

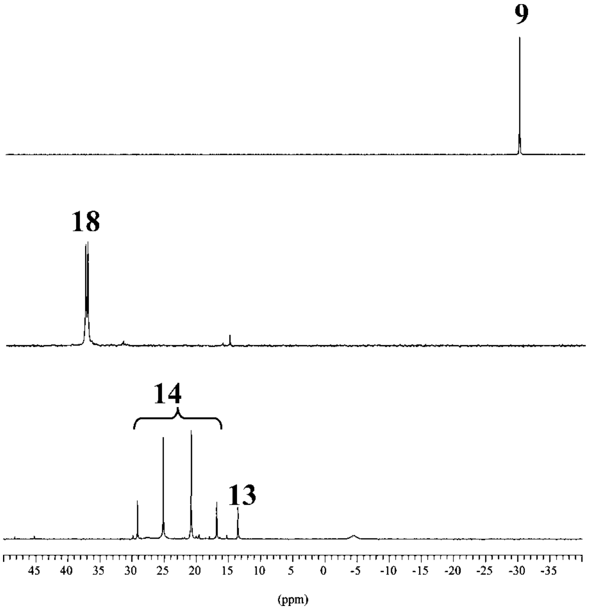
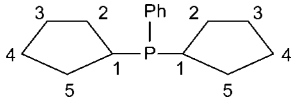


Figure 4. Trace a: ^{31}P{^{1}H} NMR spectrum of **9** in CDCl$_3$, Trace b: ^{31}P{^{1}H} NMR spectrum recorded after addition of 1 equiv of Pd$_2$(dba)$_3$ to the above solution. Trace c: ^{31}P{^{1}H} NMR spectrum recorded after subsequent addition of an equivalent amount of PPh$_3$.

The following shows the legend for ^{13}C NMR assignments:



[MoI(CO)$_3$]$_2$[(η^5-C$_5$H$_4$)P(Ph)(η^5-C$_5$H$_4$)] (9). A 250 mL Schlenk flask was charged with 3.57 g (0.013 mol) of thallium cyclopentadienide. After three cycles of vacuum/argon, 50 mL of Et$_2$O was added to the flask and the solution was treated with 0.6 mL (0.0043 mol) of dichlorophenylphosphine. The reaction mixture was stirred for 1 h at room temperature. During this time, thallium chloride precipitated as a white powder. The resulting suspension was filtered, and the solid residue was washed three times with 20 mL portions of Et$_2$O. After removal of the solvent, the resulting pale yellow oil was dissolved in 50 mL of THF. To this solution, cooled to 0 °C in an ice bath, was added dropwise *n*BuLi (1.6 M solution in hexanes) (5.6 mL, 0.009 mol). Afterward, 2.75 g (0.009 mol) of Mo(CH$_3$CN)$_3$(CO)$_3$ was added in one portion, causing an immediate color change from yellow to deep green. After being stirred overnight at room temperature, the reaction was completed by refluxing for 2 h. The reaction mixture was allowed to cool to room temperature and then was treated with 2.54 g (0.009 mol) of solid 1,2-diiodoethane. The resulting deep red solution was stirred for 1 h at room temperature then Celite (8 g) was added and the solvent was removed under vacuum. The residue was filtered over a silica gel pad with 1:1 *n*-hexane/dichloromethane as eluting solution. After concentration to a small volume, a red solid was obtained by adding *n*-pentane, which was filtered on a sintered-glass frit, washed with *n*-pentane, and then dried under vacuum to give 2.31 g (63%) of pure **9**.

The recrystallization from CH$_2$Cl$_2$/*n*-pentane (by liquid diffusion) at room temperature gave dark red brick crystals, suitable for single-crystal X-ray diffraction.

^{1}H NMR (CDCl$_3$, ppm): δ 7.60–7.44 (m, 5H, *Ph*), 5.83 (m, 2H), 5.72 (m, 2H), 5.68 (m, 2H), 5.34 (m, 2H) (*Cp*). ^{31}P NMR (CDCl$_3$, ppm): δ −30.1 (s). ^{13}C NMR (CDCl$_3$, ppm): δ 234.5, 219.2, 218.7

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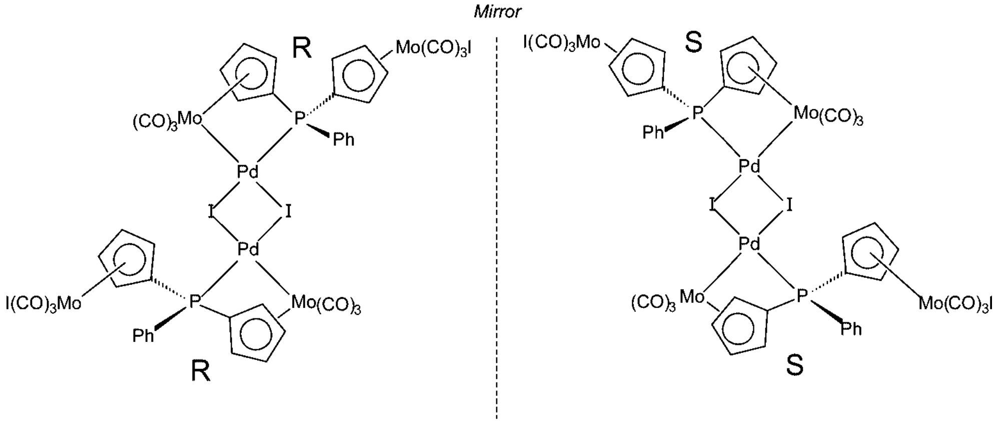
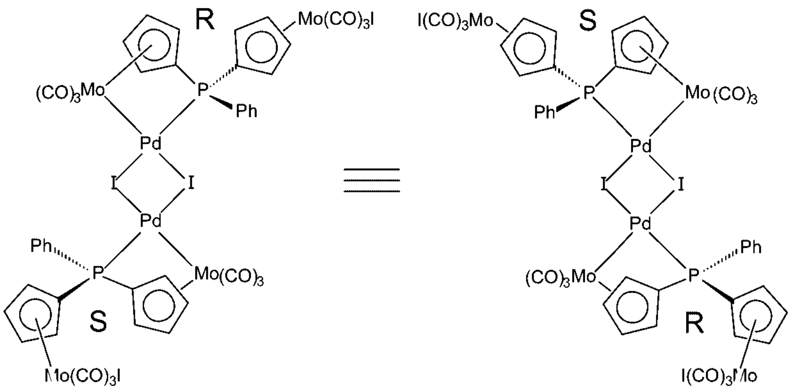
(26) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

Chart 4



18a



18b

(*CO*), 134.2, 133.8, 133.6, 131.2, 129.4, 129.2 (*Ph*), 105.4 (d, J = 21.4 Hz, C_1), 100.6 (d, J = 15.9 Hz, C_2 or C_5), 98.9 (s, C_3 or C_4), 96.4 (d, J = 2.4 Hz, C_3 or C_4), 96.1 (d, J = 10.4 Hz, C_2 or C_5). IR (CH_2Cl_2, cm^{-1}): 2044 (s), 1971 (s) (ν_{CO}). MS (15V, ESP^+) = 766 $(M + H - 3CO)^+$, 696 $(M - I - CO)^+$. Anal. Calcd for $C_{22}H_{13}I_2Mo_2O_6P$ (850.00): C, 31.09; H, 1.54. Found: C, 31.11; H, 1.60.

$[WI(CO)_3]_2[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)]$ (10). Complex **10** was prepared by employing a procedure analogous to that described above for **9**, except for using 2.53 g (0.0065 mol) of $W(CH_3CN)_3(CO)_3$, 3.18 g (0.011 mol) of CpTl, 0.4 mL (0.0029 mol) of dichlorophenylphosphine, 3.9 mL (0.0062 mol) of *n*BuLi (1.6 M solution in hexanes), and 1.83 g (0.0065 mol) of 1,2-diiodoethane. The crude mixture was adsorbed on Celite (5 g) and filtered over a silica gel pad with a 1:1 *n*-hexane/dichloromethane eluting solution. After concentration to a small volume, the addition of *n*-pentane caused the precipitation of a dark red solid. The precipitate was filtered on a sintered-glass frit, washed with *n*-pentane, and dried under vacuum to give 2.08 g (68%) of pure **10**.

^1H NMR ($CDCl_3$, ppm): δ 7.58–7.45 (m, 5H, *Ph*), 5.97 (m, 2H), 5.85 (m, 2H), 5.73 (m, 2H), 5.41 (m, 2H) (*Cp*); ^{31}P NMR ($CDCl_3$, ppm): δ −25.9 (s). ^{13}C NMR ($CDCl_3$, ppm): δ 222.2, 208.0, 207.4 (*CO*), 134.0 (d, J 23.3 Hz, *o-Ph*), 133.5 (d, J 9.0 Hz, *ipso-Ph*), 131.5 (s, *p-Ph*), 129.5 (d, J = 9.0 Hz, *m-Ph*), 102.7 (d, J = 19.8 Hz, C_1), 98.9 (d, J = 14.4 Hz, C_2 or C_5), 98.2 (s, C_3 or C_4), 95.3 (s, C_3 or C_4), 94.1 (d, J = 10.8 Hz, C_2 or C_5). IR (CH_2Cl_2, cm^{-1}): 2038 (s), 1957 (s) (ν_{CO}). MS (15V, ESP^+): *939* $(M - I + K)^+$. Anal. Calcd for $C_{22}H_{13}I_2O_6PW_2$ (1025.82): C, 25.76; H, 1.28. Found: C, 25.73; H, 1.31.

$MoI(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3MoPd(PPh_3)I$ (14). A 100 mL Schlenk flask was charged with 0.50 g (0.26 mmol) of **18**, 0.136 g (0.52 mmol) of PPh_3, and 40 mL of THF. The reaction mixture was stirred for 15 min at room temperature. After the solvent was removed under reduced pressure, the residue was redissolved in dichloromethane and precipitated with *n*-pentane. The red powder obtained was found to contain **14** together with 15–20% of *trans*-$(PPh_3)_2PdI_2$ (**13**).[27]

^1H NMR ($CDCl_3$, ppm): δ 8.15 (m, 2H, *o*-Ph), 7.68–7.43 (m, 18H, *Ph*), 6.33 (m, 1H), 6.02 (m, 1H), 5.78 (m, 2H), 5.52 (m, 1H), 5.43 (m, 1H), 5.24 (m, 1H), 4.06 (m, 1H) (*Cp*). ^{31}P NMR ($CDCl_3$, ppm): AB spin system centered at δ 21.5 (J_{PP} = 491 Hz). IR (CH_2Cl_2, cm^{-1}): 2048 (m), 1972 (s), 1898 (m), 1879 (m) (ν_{CO}). MS (15V, ESP^+): *1092* $(M - I)^+$.

Contamination of compound **14** by complex **13** prevented an accurate elemental analysis (see trace c in Figure 4).

$WI(CO)_3[(\eta^5\text{-}C_5H_4)P(Ph)(\eta^5\text{-}C_5H_4)](CO)_3WPd(PPh_3)I$ (15). A 100 mL Schlenk flask was charged with 0.50 g (0.49 mmol) of **10** and 0.57 g (0.49 mmol) of $Pd(PPh_3)_4$. After three cycles of vacuum/argon, 30 mL of THF was added to the flask and the resulting dark solution was stirred for 30 min at room temperature. The crude mixture was adsorbed on Celite and purified by chromatography on a silica column (50 × 5 cm). The last fraction eluted with dichloromethane gave, after removal of the solvent, **15** as a crystalline red solid, contaminated by a small amount (<1%) of *trans*-$(PPh_3)_2PdI_2$ (**13**).[27]

^1H NMR ($CDCl_3$, ppm): δ 8.15 (m, 2H, *o*-Ph), 7.72–7.36 (m, 18H, *Ph*), 6.27 (m, 1H), 5.96 (m, 1H), 5.91 (m, 2H), 5.52 (m, 1H), 5.40 (m, 2H), 4.16 (m, 1H) (*Cp*). ^{31}P NMR ($CDCl_3$, ppm): AB

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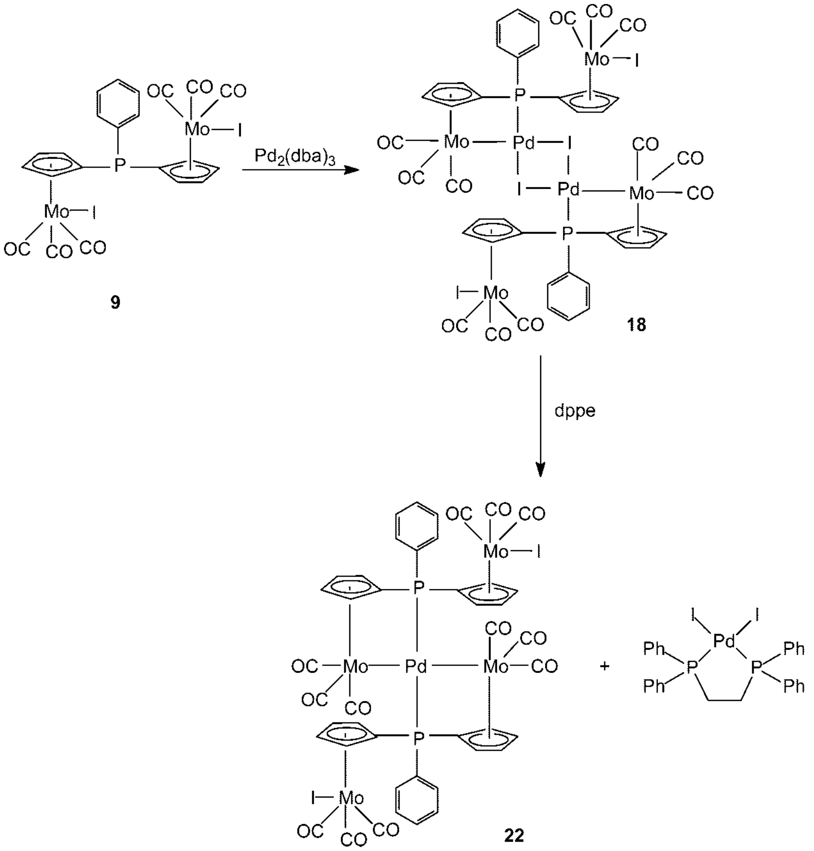
[27] Isolation of analytically pure **14** was impaired by two factors: (i) under chromatographic conditions **14** loses PPh_3 generating **18**, and (ii) even by operating under a strict 1/1 stoichiometric ratio of PPh_3 and **18**, the contamination by complex **13** is unavoidable. On the other hand, detachment of PPh_3 from the W analogue is more difficult, thus chromatographic purification affording pure **15** is possible.

Scheme 5



spin system centered at δ 17.6 (J_{PP} = 487 Hz). ^{13}C NMR (CDCl$_3$, ppm): δ 223.9, 220.5, 214.0, 212.6, 207.6, 207.2 (*C*O), 136.3–127.5 (*Ph*), 105.0, 102.7, 102.6 (d, J = 19.7 Hz), 102.2 (d, J = 19.7 Hz), 98.9, 92.3–90.0, 58.9 (d, J = 28.7 Hz), 58.8 (d, J = 28.7 Hz) (*Cp*). IR (CH$_2$Cl$_2$, cm^{-1}): 2040 (s), 1965 (s), 1890 (sh), 1869 (s). MS (15V, ESP$^+$): *1268* (M − I)$^+$.

This preparation also gave complex **13** (ca. 1%) thus preventing an accurate elemental analisys of **15** (^{31}P{^{1}H} NMR spectrum in the Supporting Information shows contamination of **15** by **13**).

It is worth noting that the first fractions eluted contained a mixture of **15** together with the halobridged dimer **19**. The latter complex was not isolated, but the Mo analogue was isolated and unambiguously identified (see below).

^{31}P NMR (CDCl$_3$, ppm): δ 27.0 (s), 26.6 (s) (**19**), AB spin system centered at δ 17.6 (J_{PP} = 487 Hz) (**15**).

{MoI(CO)$_3$[(η^5-C$_5$H$_4$)P(Ph)(η^5-C$_5$H$_4$)](CO)$_3$MoPd}(μ-I$_2$){PdMo(CO)$_3$[(η^5-C$_5$H$_4$)P(Ph)(η^5-C$_5$H$_4$)](CO)$_3$MoI} (18). A 100 mL Schlenk flask was charged with 0.70 g (0.82 mmol) of **9** and 0.38 g (0.41 mmol) of Pd$_2$(dba)$_3$. After three cycles of vacuum/argon, 20 mL of THF was added to the flask and the resulting dark solution was stirred for 15 min at room temperature. After the solvent was removed under reduced pressure, the residue was redissolved in a small amount of dichloromethane. Upon addition of *n*-pentane a red-brown powder precipitated, which was collected by filtration on a sintered-glass frit, washed repeatedly with *n*-pentane to eliminate the residual dba ligand, and then chromatographed on silica column (30 × 5 cm). Elution with a 3:7 mixture of *n*-hexane/dichloromethane produced a little red band, which was discarded. The elution was continued with dichloromethane to obtain a dark red band, which was collected to give 0.43 g (55%) of pure **18** as red-brown fine powder.

^{1}H NMR (CDCl$_3$, ppm): δ 8.26 (m, 4H, *o*-Ph), 7.59–7.46 (m, 6H, *m,p*-Ph), 6.19 (m, 1H), 6.12 (m, 1H), 5.96 (m, 2H), 5.78 (m, 1H), 5.75 (m, 1H), 5.70 (m, 1H), 5.67 (m, 1H), 5.54 (m, 2H), 5.46 (m, 2H), 5.21 (m, 1H), 5.06 (m, 1H), 4.20 (m, 1H), 4.16 (m, 1H) (*Cp*). ^{31}P NMR (CDCl$_3$, ppm): 37.7 (s), 37.3 (s). ^{13}C NMR (CDCl$_3$, ppm): δ 231.7, 231.0, 218.5, 218.2, 217.6, 217.4 (*C*O), 148.9, 148.7, 142.2–141.8, 136.3–128.4 (*Ph*), 105.7, 105.1, 102.7, 102.6, 94.7–91.5, 68.0, 47.0 (d, J = 16.2 Hz), 43.3 (d, J = 14.4 Hz) (*Cp*). IR (CH$_2$Cl$_2$, cm^{-1}): 2050 (s), 1981 (s), 1903 (s) (ν_{CO}). MS (15V, ESP$^+$): *883* (M − 4CO + K)$^+$. Anal. Calcd for C$_{44}$H$_{26}$I$_2$Mo$_4$O$_{12}$P$_2$Pd (1552.62): C, 34.04; H, 1.69. Found: C, 34.10; H, 1.76.

X-ray Data Collection and Refinement of [MoI(CO)$_3$]$_2$[(η^5-C$_5$H$_4$)P(Ph)(η^5-C$_5$H$_4$)] (9). A parallelepiped crystal with dimension 0.375 × 0.125 × 0.075 mm^3 was used for the data collection. Experimental data were recorded at room temperature (20 °C) on an Enraf-Nonius CAD4. A set of 25 carefully centered reflections in the range 8.25° $\leq \theta \geq$ 10.45° was used for determining the lattice constants. As a general procedure, the intensity of three standard reflections was measured periodically every 200 reflections for orientation and intensity control. This procedure did not reveal decay of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were taken from AJC Wilson[28] with anomalous dispersion corrections taken from ref 29. An empirical absorptions correction was applied via Ψ scan with correction factors in the range 0.7669−0.5524. The computational work was carried out by using the program SHELX97.[30] Final atomic coordinates of all atoms and structure factors are available on request from the authors and are provided as Supporting Information. The structure was solved by direct methods by using the SIR97 program.[31] The refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters then with anisotropic thermal parameters for all the atoms. Hydrogen

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(28) Wilson. A. J.C. *International Tables for X-Ray Crystallography*; Kluver Academic: Dordrecht, The Netherlands, The Netherlands, 1992; *Vol. C*, p 500.

(29) Wilson. A. J. C. *International Tables for X-Ray Crystallography*; Kluver Academic: Dordrecht, The Netherlands, 1992; *Vol. C*, p 219.

(30) Sheldrick, G. M. *SHELX-97. Program for Structure Refinement*, Release 97-2; University of Göttingen: Göttingen, Germany, 1997.

were introduced at calculated positions. The phenyl ring was treated as a rigid body with D_{6h} symmetry, and the hydrogen atoms were allowed to ride on the attached carbon atoms.

Supporting Information Available: Full tables of crystal data, atomic coordinates, thermal parameters, bond lengths and angles, and a CIF file for **9** and $^{31}P\{^{1}H\}$ NMR spectrum showing contamination of **15** by **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701221P

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(31) (A) Altomare, M. C.; Burla, M.; Camalli, G.; Cascarano, C.; Giacovazzo, A.; Guagliardi, G.; Polidori, R.; Spagna, J. *Appl. Cryst.* **1999**, *32*, 115–119.