Carbon−Carbon Coupling Reactions between Metallacarbynes Cp(CO)$_2$M≡CR and Cyclopalladated Ligands: Synthesis of a Novel Class of Palladium *μ*-Alkylidene Complexes

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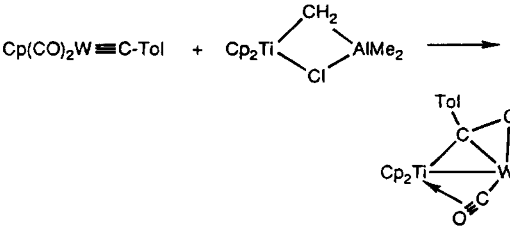
The carbyne carbon atom of metallacarbynes such as (η^5-C$_5$H$_5$)(CO)$_2$M≡CR (where M = Mo, W and R = *p*-tolyl, 4-*tert*-butylphenyl, 2,6-dimethylphenyl, 1-cyclopentenyl) is readily coupled with the palladated carbon atom of various cyclopalladated compounds. This reaction affords good to excellent yields of novel *μ*-alkylidene complexes whose structure is maintained irrespective of the palladated ligand employed. For example, the reaction of (η^5-C$_5$H$_5$)(CO)$_2$-Mo≡C-*p*-Tol with [2-Me$_2$NCH$_2$C$_6$H$_4$PdCl]$_2$ affords [2-Me$_2$NCH$_2$C$_6$H$_4$(η^3-{*μ*-C(*p*-Tol)Mo(*μ*-CO)}-C$_5$H$_5$(CO)PdCl].

Introduction

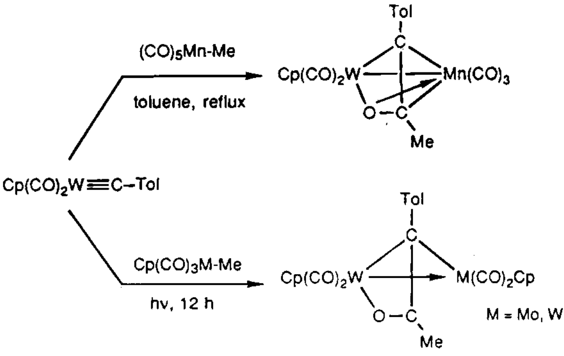
Carbon−carbon coupling reactions of metallacarbynes (of the type L$_5$M≡CR, M = d^5 metal) are well-known, although the most general reactions occur mainly in the presence of three types of reagents: tertiary phosphines, protic acids, and alkynes.[1] Tertiary phosphines induce coupling between the carbyne ligand C(R) and a carbonyl ligand, resulting in ketenyl complexes. Protonation leads to the coupling of two carbyne ligands to form bimetallic complexes with bridging alkyne ligands. Alkynes react in the presence of protons to form a series of naphthol ligands, which can be easily separated from the metal.

C−C coupling reactions between these metallacarbynes and organometallic substrates are much less common, and no truly general reaction has yet been reported. The known examples include the phenyl and alkyl complexes Cr(Ph)$_3$(thf)$_3$ and ZnR$_2$ (R = Ph, Pr, CH$_2$-4-Tol)[2] and the bimetallic Tebbe reagent. This last compound transfers its bridging methylene group onto the carbyne carbon, which corresponds to the formal insertion of the carbon atom of the triple bond into the titanium−carbon bond (eq 1).[3a]



(1)

Somewhat more general is the reaction with methyl complexes of group 6 and 7 metals, which leads to the formation of bridging acyl carbene ligands (eq 2).[3b]



(2)

Our group has been interested in the reactivity of the Pd−C bond of cyclopalladated complexes with a tertiary amine as a donor atom. Alkynes have been observed to insert one to three times into the palladium−carbon bond, leading to interesting vinyl, butadienyl, and cyclopentadienyl complexes, respectively.[4] Given the well-known isolobal analogy between alkynes and metallacarbynes,[5] it appeared promising to investigate

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[1] For leading reviews on the reactivity of metallacarbyne compounds, see: Fischer, H. *Carbyne Complexes*; VCH Verlagsgesellschaft: Weinheim, Germany, 1988; p 114. Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227.

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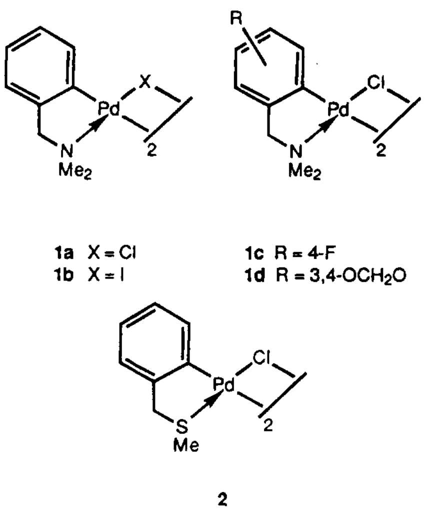
Chart 1



1a X = Cl
1b X = I
1c R = 4-F
1d R = 3,4-OCH$_2$O
2

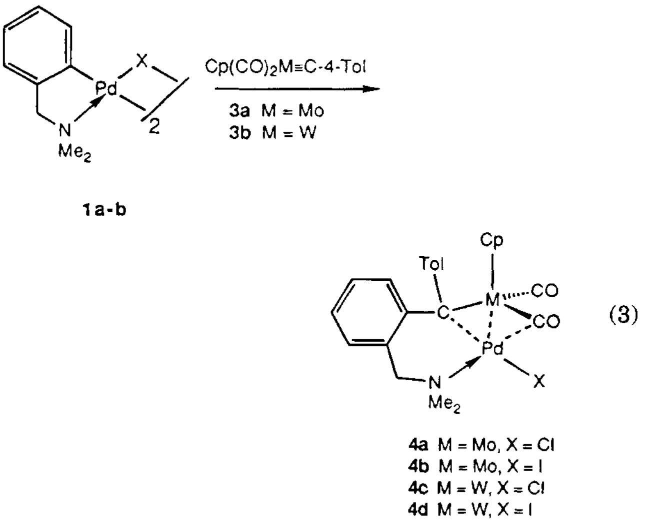
whether metallacarbynes would react with cyclopalladated compounds.

In this paper we present results from the reaction between the metallacarbynes Cp(CO)$_2$M≡CR (M = group 6 metal) and a series of cyclometalated complexes of palladium. This leads in all cases to the formal insertion of the triple bond into the palladium–carbon bond.

Reactions with Cyclopalladated Dimethylbenzylamine and Methyl Benzyl Sulfide Ligands

Influence of the Carbyne Metal and the Anionic Palladium Substituent. Compounds **1a** and **2** (Chart 1) are already known to react with alkynes, the former much more readily.[6–8]

A 2-equiv amount of the metallacarbynes Cp(CO)$_2$M≡C-4-Tol (**3a**, M = Mo; **3b**, M = W) reacts smoothly with the dmba complexes **1a,b** to form the novel bimetallic species [Cp(CO)(μ-CO)M][μ-C(4-Tol)(dmba)][Pd(X)] (**4a–d**; eq 3). These complexes have been characterized as the first palladium μ-alkylidene complexes obtained with simple cyclopentadienyl metallacarbynes.[9a] The new carbon–carbon bond results from the formal insertion of the metal–carbon triple bond into the palladium–carbon σ bond.



1a-b

4a M = Mo, X = Cl
4b M = Mo, X = I
4c M = W, X = Cl
4d M = W, X = I

All reactions proceed at room temperature in dichloromethane, and the complexes **4a–d** are obtained in 30 min to 2 h in very good yields (85–95%). The reaction is surprisingly simple and selective, since no other products can be detected.

These reactions can be followed by infrared spectroscopy, since the disappearance of the carbonyl stretching frequencies of the metallacarbynes is easily monitored. IR revealed that the molybdenum metallacarbyne **3a** usually reacts faster than its tungsten analogue **3b**. Similarly, the reaction between **3a** and the iodide complex **1b** is faster than the reaction between **3a** and the chloride complex **1a**. However, the differences in the total reaction time are relatively small.

In contrast, when the dmba complex **1b** is reacted with the chromium metallacarbyne Cp(CO)$_2$Cr≡C-4-Tol, entirely different products are obtained which have not yet been characterized.

The chloride-bridged dimer **1a** can be easily converted into the cationic cyclopalladated complex [Pd(dmba)(MeCN)$_2$][BF$_4$] (**5**) by reacting it with 2 equiv of silver tetrafluoroborate in the presence of acetonitrile.[6] Complex **5** reacts sith the metallacarbyne **3b**, affording a bimetallic cationic product. The addition of 1 equiv of dimethylphenylphosphine to the reaction mixture allows for the isolation of the cationic μ-alkylidene {[Cp(CO)(μ-CO)μ-W][μ-C(4-Tol)(dmba)][Pd(PMe$_2$Ph)]}BF$_4$ (**4e**) in 92% yield. The cationic complex **5** reacts about as fast as the dimeric iodide-bridged complex **1b**.

Thus, it seems that, apart from the chromium metallacarbyne, the halide substituent in **1** and also the metal in the metallacarbynes **3** can be easily varied, without greatly affecting the course of the reaction.

Influence of the Two-Electron-Donor Atom. Between the dmba complex **1a** and the bms complex **2**, only the nature of the two-electron-donor atom changes (N, S), although this has considerable consequences for the related alkyne insertion. While **1a** is fairly reactive toward nonactivated alkynes,[6] complex **2** must be treated under more vigorous conditions[8] to obtain an insertion product. When **2** is reacted with 2 equiv of the metallacarbynes **3a,b** in dichloromethane, a rapid reaction takes place, leading to a deep red-brown solution; the color of the solution then lightens and, after only 1 min, the bimetallic complexes [Cp(CO)(μ-CO)M][μ-C(4-Tol)(bms)][Pd(Cl)] (**6**) can be isolated in good yield (75–85%; Chart 2). This reaction is notably faster than the analogous reaction between **1a** and **3b** (2 h).

Apparently, the nature of the two-electron-donor atom may greatly influence the overall reaction rate.

Influence of the Substituents on the Carbyne Carbon. Changing the nature of the substituent on the

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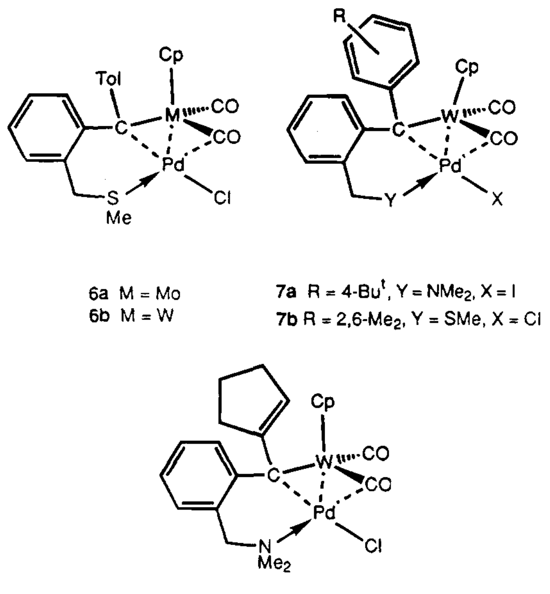
Chart 2

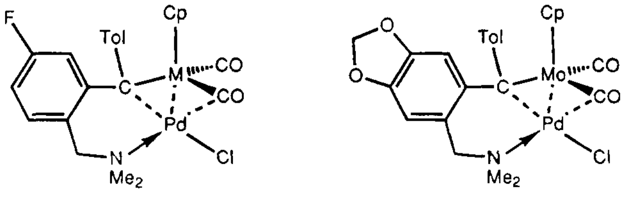


6a M = Mo
6b M = W

7a R = 4-Bu^t, Y = NMe$_2$, X = I
7b R = 2,6-Me$_2$, Y = SMe, X = Cl

7c

Chart 3



8a M = Mo
8b M = W

9

carbyne carbon may influence the course of the coupling reaction with cyclopalladated ligands, and for this purpose, the metallacarbynes $Cp(CO)_2W{\equiv}C\text{-}4\text{-}C_6H_4{}^tBu$ (**3c**) and $Cp(CO)_2W{\equiv}C\text{-}1,2\text{-}C_6H_3Me_2$ (**3d**) were prepared. The metallacarbyne **3c** displays a reactivity strictly analogous to that of the *p*-tolyl metallacarbyne **3b**, and from the reaction with the dmba complex **1b** the expected product [Cp(CO)(μ-CO)W][μ-C(4-$C_6H_4Bu^t$) (dmba)][Pd(I)] (**7a**) is obtained in high yield (90%). The electronic differences between the *p*-methyl and the *p*-*t*-Bu group are negligible in this reaction.

In contrast, the reactivity of the 2,6-xylyl metallacarbyne **3d** is remarkably different from that of **3b**. The major difference between the metallacarbynes **3b** and **3d** is the steric bulk of the *o*-methyl groups in the latter, and it appears that precisely this steric difference is important since it may hinder the interaction between the metallacarbynes and the cyclopalladated complexes. Two equivalents of **3d** reacts with the bms complex **2** to give the bimetallic product [Cp(CO)(μ-CO)W][μ-C(2,6-$C_6H_3Me_2$)(bms)][Pd(Cl)] (**7b**) in 79% yield, but the reaction takes much longer to reach completion (about 5 h) than the reaction between **2** and **3b**.

All metallacarbynes **3a**–**d** possess an aromatic ring on the carbyne carbon, but other metallacarbynes with alkyl substituents can be prepared. Under the same conditions as for **3a**–**d**, the methyl metallacarbyne $Cp(CO)_2W{\equiv}CMe$ reacts with the dmba complexes **1**; unfortunately, the outcome of this reaction is totally different and the products have not been characterized. It is unlikely that only the electronic differences between **3b** and the methyl metallacarbyne are responsible for this unexpected result. We suspect that the decomposition observed is related to the presence of a hydrogen substituent α to the carbyne carbon.

To circumvent this problem, the metallacarbyne $Cp(CO)_2W{\equiv}C\text{-cyclo-1-}C_5H_7$ (**3e**) was prepared, which contains a cyclopentenyl ligand devoid of any hydrogen atom α to the carbyne carbon. Indeed, 2 equiv of **3e** reacts in the normal way with **1a** via a deep red-brown intermediate, to afford the bimetallic complex [Cp(CO)(μ-CO)W][μ-C(cyclo-1-C_5H_7)(dmba)[[Pd(Cl)] (**7c**) in 87% yield. It seems that the alkenyl metallacarbyne **3e** reacts in much the same way as the metallacarbynes **3a**–**c**, which promises further extension of the reaction to other metallacarbynes with a nonaromatic substituent. Apparently, the size of the carbyne substituent is decisive in these coupling reactions, while the electronic nature of the carbyne carbon is relatively unimportant.

Electronic Influence of Substituents on the Ring of the dmba Ligand. Since the new C–C bond in the bimetallic products **4** has been formed between the carbyne carbon and the formerly metalated carbon, an aspect to be considered is the electron density on the aromatic ring of the cyclopalladated ligand. Complexes **1c,d** have been used for this purpose, since they possess substituents at position 3 and 4 on the aromatic ring of the dmba ligand, which have opposite inductive effects (Chart 1).

Complexes **1c,d** each react with 2 equiv of the metallacarbynes **3a,b** to give the expected complexes [Cp(CO)(μ-CO)M][μ-C(4-Tol)(3-F-dmba)][Pd(Cl)] (**8**) and [Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(3,4-OCH_2O-dmba)][Pd(Cl)] (**9**) in high yields (75–90%) (Chart 3). However, no notable difference in the total reaction time has been observed, which allows us to conclude that within this range of substituents their electronic effects can be neglected in this reaction.

Reactions with other Cyclopalladated Ligands

Now that the scope of the reaction for the model starting compounds containing the ligands dmba (**1**) and bms (**2**) has been established, more important changes in the cyclopalladated ligands need to be studied. A number of cyclopalladated ligands are known to react with alkynes, and in these reactions very different products are obtained, depending on both the geometry of the metallacycle and the nature of both the metalated carbon and the donor atom. It can therefore be expected that the cyclopalladated ligand will have a major influence on the course of the coupling reaction.

Six representative complexes were chosen for this purpose (see Chart 4). The complexes derived from 8-methylquinoline (8mquin; **10**),[6,7] benzo[*h*]quinoline (bhq; **11**),[7,10] 8-ethylquinoline (8equin; **12**),[11] 2-benzylpyridine (bzpy; **13**),[12] 2-phenyl-*N*,*N*-dimethylaniline (bpdma; **14**),[13] and 2-biphenyl methyl sulfide (bpms; **15**)[13]

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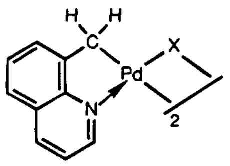
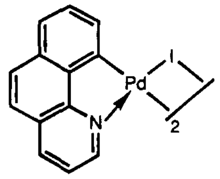
Chart 4



10a X = Cl
10b X = I



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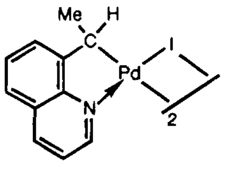

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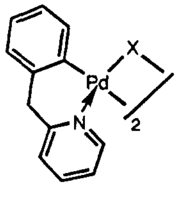
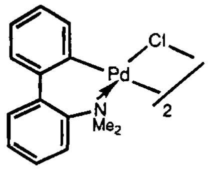


13a X = Cl
13b X = I
13c X = OAc



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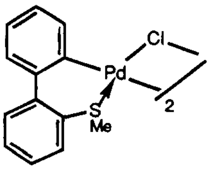

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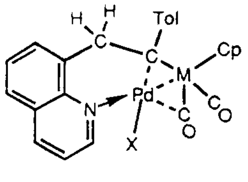
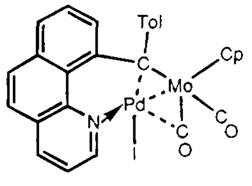
Chart 5



16a M = W, X = I
16b M = Mo, X = Cl
16c M = Mo, X = I



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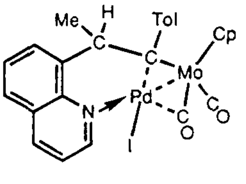

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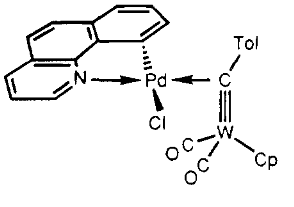

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are all known for their insertion reactions with disubstituted alkynes. For these reactions either an organometallic or an organic product can be isolated, the latter resulting from an insertion reaction followed by loss of the palladium.

Rigid Five-Membered Metallacycles: the Quinoline Ligands. The cyclopalladated complexes of the quinoline ligands **10**–**12** are five-membered metallacycles similar to the dmba complexes **1**. However, due to the rigidity of the quinoline ring system, their reactivity with alkynes is rather different from that of complexes **1**. The 8mquin complexes **10** undergo normal insertion reactions with alkynes, whereas the bhq and 8equin complexes **11** and **12** react only with electrophilic alkynes such as hexafluorobut-2-yne[7] or dimethyl acetylenedicarboxylate, respectively.[11]

Adding 2 equiv of the tungsten metallacarbyne **3b** to a solution of the 8mquin chloride complex **10a** results in an instantaneous color change of the solution from orange to deep red-brown. Upon standing at room temperature, a slow decomposition of the solution was observed, but no bimetallic complexes such as **4** could be isolated.

When the iodide complex **10b** is reacted with **3b** in the same way, the deep red-brown color gradually disappears over 30 min and the lighter color of the bimetallic complex [Cp(CO)(μ-CO)W][μ-C(4-Tol)(8mquin)]-[Pd(I)] (**16a**) is obtained, which is isolated in 59% yield. This yield is notably lower than that obtained with the dmba complex **1b**, since other, undefined products are formed at the same time.

Apparently, the molybdenum metallacarbyne **3a** is more reactive than its tungsten analogue **3b**, since it reacts with both the chloride (**10a**) and iodide (**10b**) complexes to give the μ-alkylidene complexes [Cp(CO)-(μ-CO)Mo][μ-C(4-Tol)(8mquin)][Pd(X)] (**16b,c**) in about 60% yield.

The chloride-bridged analogue of the bhq complex **11** is less reactive than the 8mquin complex **10a**. In the reaction with the metallacarbyne **3b**, a deep red-brown coordination complex is formed that is stable enough to be isolated. It has been characterized by an X-ray diffraction study as the μ-alkylidyne complex [Cp-$(CO)_2$W][μ-C(4-Tol)][Pd(bhq)Cl] (**19**). In this complex, no new carbon–carbon bond has yet been formed. We have published its crystal structure,[9a] and it showed that the metallacarbyne is simply coordinated to the palladium center as an unusual ligand via its carbyne carbon, whereas the M≡C unit is perpendicular to the coordination plane of the palladium atom. This compound will be analyzed in more detail (from a structural and theoretical point of view) elsewhere.[9b]

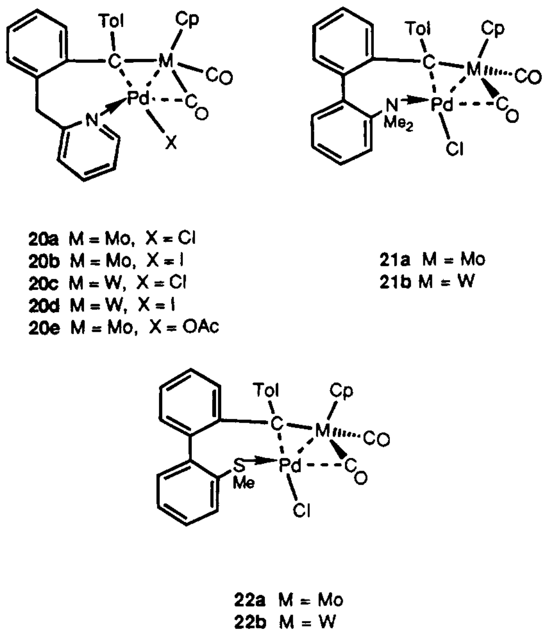
In fact, only the reaction of 2 equiv of **3a** with the iodide bhq complex **11** affords the bimetallic complex [Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bhq)][Pd(I)] (**17**) in about 4 h (72%). Immediately after the compounds are mixed, the color changes to deep red-brown and this color slowly lightens during the formation of the product **17**.

At first sight, the 8equin complex **12** seems to be very similar to the 8mquin complex **10b**, but it proved to be the least reactive of all the cyclopalladated ligands tested so far. The chloride-bridged analogue of **12** reacts with the metallacarbyne **3b** to form an unstable deep red-brown solution. Even so, the reaction between **3a** and **12** is slow, and a mixture of several products is obtained, from which the coupling product [Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(8equin)][Pd(I)] (**18**) can be extracted, albeit in low yield (23%).

Flexible Six-Membered Metallacycles: Benzylpyridine and Biphenyl Complexes. Six-membered metallacyclic complexes chosen include those derived from the ligands bzpy (**13**), bpdma (**14**), and bpms (**15**) (Chart 4).

The reaction between the bzpy chloride complex **13a** and the metallacarbynes **3a,b** is much slower (more than 15 h) than is the case for the dmba complex **1a**; however, the bimetallic complexes [Cp(CO)(μ-CO)M][μ-

Chart 6



20a M = Mo, X = Cl
20b M = Mo, X = I
20c M = W, X = Cl
20d M = W, X = I
20e M = Mo, X = OAc

21a M = Mo
21b M = W

22a M = Mo
22b M = W

C(4-Tol)(bzpy)][Pd(Cl)] (**20a,c**) are isolated in good yields (90%). The reaction is accelerated when a larger excess of metallacarbyne is used. Even faster is the reaction of the iodide complex **13b** with the metallacarbynes **3a,b**, which affords the bimetallic products [Cp(CO)(μ-CO)M][μ-C(4-Tol)(bzpy)][Pd(I)] (**20b,d**) within 30–120 min.

Addition of 2 equiv of **3a** to a solution of the acetate complex **13a** in dichloromethane induces a gradual color change, and a complex perfectly analogous to **20a** is isolated after 2 h in about 60% yield: [Cp(CO)(μ-CO)-Mo][μ-C(4-Tol)(bzpy)][Pd(OAc)] (**20e**). The overall reaction time is comparable with the total reaction time observed for the formation of **20b**, which suggests that the iodide-bridged and the acetate-bridged complexes are about equally reactive toward **3a**.

Another class of six-membered metallacycles is represented by the complexes **14** and **15** (Chart 4). The metallacarbynes **3a,b** react rapidly with the chloride bpdma complex **14**, and bimetallic products [Cp(CO)(μ-CO)M][μ-C(4-Tol)(bpdma)][Pd(Cl)] (**21**) are obtained within 30 min. The reaction is not very successful, since many side products are formed and, consequently, products **21** are isolated in yields around 30%.

The bpms complex **15** is the exact analogue of the bpdma complex **14**, in which only the nature of the donor atom is different (NMe$_2$ vs SMe). Complex **15** reacts rapidly with the metallacarbynes **3a,b**, and the expected bimetallic products [Cp(CO)(μ-CO)M][μ-C(4-Tol)(bpms)][Pd(Cl) (**22**) are obtained in good yields within 30 min (75–85%). Since the bpdma complex **14** already reacts quickly with **3a** or **3b**, the total reaction times of the formation of **21** and **22** cannot be easily compared by infrared spectroscopy. However, the remarkable difference in the isolated yields of **21** and **22** once again confirms the greater reactivity of ligands containing a sulfur donor atom, compared to their counterparts with a nitrogen atom.

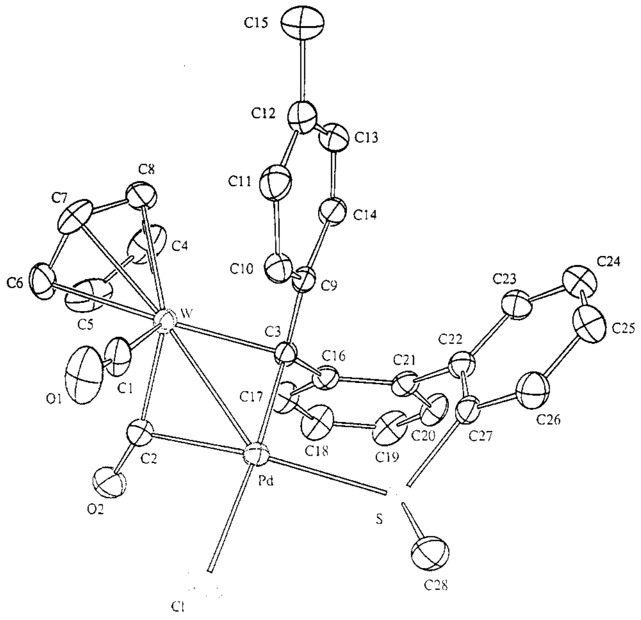


Figure 1. ORTEP diagram of [Cp(CO)(μ-CO)W][μ-C(4-Tol)(bpms)][Pd(Cl)] (**22b**). Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å), Angles (deg), and Dihedral Angles (deg) for 22b

	Bond Distances		
Pd$\cdots$C$_1$	2.964(5)	W–Pd	2.6973(3)
Pd–C$_2$	2.235(5)	W–C$_3$	2.158(4)
Pd–C$_3$	2.024(4)	W–C$_1$	1.995(5)
Pd–S	2.406(1)	W–C$_2$	2.002(4)
Pd–Cl	2.400(1)	W–Cp′^{a}	1.9806(2)
C$_1$–O$_1$	1.135(5)	C$_3$–C$_{16}$	1.483(5)
C$_2$–O$_2$	1.153(5)	C$_3$–C$_9$	1.440(6)
	Bond Angles		
C$_3$–Pd–Cl	174.1(1)	Cp′–W–C$_3$^{a}	126.64(10)
C$_2$–Pd–S	155.2(1)	C$_1$–W–C$_3$	117.4(2)
C$_3$–Pd–S	91.3(1)	C$_2$–W–C$_3$	84.4(2)
C$_3$–Pd–C$_2$	82.0(2)	C$_1$–W–C$_2$	83.8(2)
C$_2$–Pd–Cl	92.2(1)	Pd–W–C$_3$	47.7(1)
Cl–Pd–S	93.69(4)	W–C$_3$–Pd	80.3(1)
W–Pd–S	140.52(3)	W–C$_3$–C$_{16}$	137.9(3)
W–C$_1$–O$_1$	175.8(4)	W–C$_3$–C$_9$	80.9(2)
W–C$_2$–O$_2$	160.0(4)	Pd–C$_3$–C$_9$	118.2(3)
Pd–C$_2$–O$_2$	121.0(3)	Pd–C$_3$–C$_{16}$	109.3(3)
Pd–S–C$_{27}$	112.1(1)	C$_9$–C$_3$–C$_{16}$	123.6(3)
Pd–S–C$_{28}$	110.3(2)	C$_{27}$–S–C$_{28}$	103.9(2)

Dihedral Angles

plane 1	plane 2	angle
Cp′–W–C$_3$^{a}	W–C$_3$–Pd	22.75(30)
W–C$_3$–C$_9$	C$_9$–C$_{13}$	61.01(15)
W–C$_3$–C$_{16}$	C$_{16}$–C$_{21}$	168.69(66)
C$_{16}$–C$_{21}$	C$_{22}$–C$_{27}$	64.38(12)

[a] Cp′ is the centroid of η^5-C$_5$H$_5$.

Characterization of the Complexes

Solid-State Structure of [Cp(CO)(μ-CO)W][μ-C-(4-Tol)(bpms)][Pd(Cl)] (22b). To analyze one of the μ-alkylidene complexes in detail, a single crystal diffraction study has been carried out on a crystal of complex **22b**. Figure 1 shows its ORTEP diagram with the corresponding atom labeling scheme, and selected interatomic distances, angles, and dihedral angles are given in Table 1.

It is at once clear from Figure 1 that the former palladium–carbon bond Pd–C$_{16}$ has been broken and that a new carbon–carbon bond has been formed between C$_3$ and C$_{16}$. The molecule can be formally considered as the sum of two parts, the fragment Cp(CO)$_2$W–C$_3$–[C$_9$-C$_{15}$] derived from the metallacarbyne

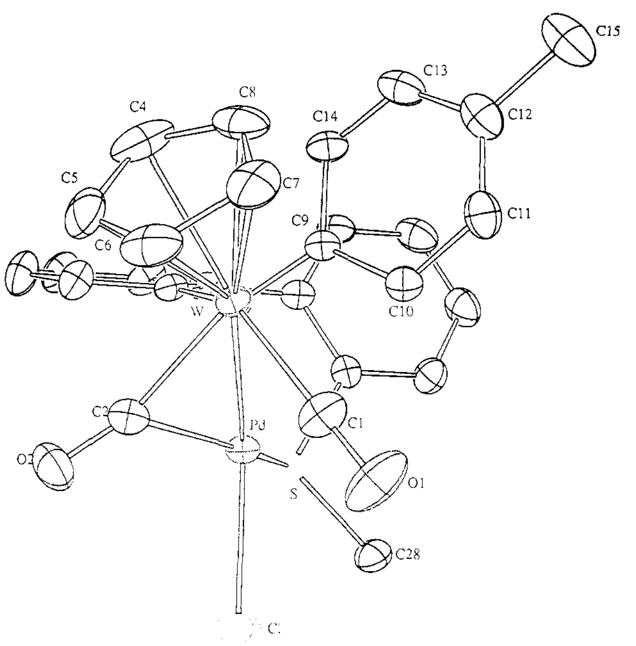


Figure 2. ORTEP drawing of **22b**, viewed along the C_3–W axis from W to C_3 (C_3 is obscured by W, 50% ellipsoids). Hydrogen atoms have been omitted for clarity.

3b and the fragment $[C_{16}-C_{28}]Pd(S)Cl$, derived from the palladium dimer **15**.

Description of the Structure of 22b. The palladium atom is within bonding distance of the five atoms C_2, W, C_3, S, and Cl. The last three atoms are arranged around palladium in a normal square-planar arrangement, with mutual angles close to 90 or 180°. The atoms C_2 and W seem to occupy together the fourth coordination site of palladium. The carbon C_2, however, is closer to the position opposite to S than the tungsten atom (C_2–Pd = 2.235(5) Å, C_2–Pd–S = 155.21(1)°, and W–Pd–S = 140.52(3)°).

The view of **22b** from W to C_3 along the C_3–W axis shows a small dihedral angle between the planes Cp′–W–C_3 and W–C_3–Pd (22.75(30)°; Figure 2). The result of this torsion is that C_2 comes close enough to palladium to interact, while the other carbonyl carbon C_1 is turned away from palladium (Pd–C_1 = 2.964(5) Å). The angles W–C_2–O_2 (160.0(4)°) and Pd–C_2–O_2 (121.0(3)°) indicate that C_2O_2 is a semibridging carbonyl ligand.

The real nature of **22b** is revealed by the geometry of the bridging carbon C_3, which is strongly bound to both metals W and Pd and to both aryl rings via the ipso carbons C_9 and C_{16}. Whereas the Pd–C_3 distance (2.024(4) Å) is on the order of covalent Pd–C σ bonds (1.99–2.15 Å),[15] the W–C_3 distance (2.158(4) Å) is more difficult to interpret. It is longer than the W–C bond in a typical Fischer metallacarbene (2.04 Å for $(CO)_5W{=}C(OMe)Ph$)[16] but much shorter than the W–C bond of the same metallacarbene bridging a Pt(0) fragment (2.48 Å).[17]

The angles around C_3 are not those expected for a normal sp^2 or sp^3 carbon, but the "internal" angle W–C_3–Pd (80.3(1)°) falls into the range found in μ-alkylidene complexes (M–C–M′ = 76–81°).[18] The "external" angle C_9–C_3–C_{16} (123.6°) is larger than the upper limit indicated for μ-alkylidenes (R–C–R′ = 105 ± 13°),[18] but it is known that this angle is rather dependent on the bulk of the carbene substituents. Moreover, the fact that one of these substituents is cyclopalladated will only add to the distortion of the angles around C_3. The W–Pd distance (2.6973(3) Å) is shorter than the W–Pt distance in a comparable dimetallacyclopropane complex (2.86 Å),[17] and it coincides with values that are usually found for a bonding metal–metal interaction (2.40–3.20 Å).[18]

Table 2. Selected Spectral Data for μ-Alkylidene Complexes with Different Cyclopalladated Ligands

	IR (cm^{-1})[a] ν_{CO}		^1H NMR (ppm)[b] ∂	
compd	ν_1	ν_2	Cp (s)	*p*-Tol: C_6H_4;[c] 4-Me (s)
4a	1975	1829	4.63	6.74; 2.32
6a	1975	1839	4.65	6.71, 7.07; 2.34
16c	1972	1812	4.55	*d*; 2.23
17	1973	1822	4.73	6.85; 2.22
18	1975	1820	4.56	7.07; 2.22
20a	1983	1847	4.60	6.68; 2.32
21a	1973	1822	4.42	6.49, 6.77; 2.19
22a	1975	1831	4.47	6.61, 6.79; 2.20

	^{13}C NMR (ppm) ∂				
compd	Cp	CO	μ-C	C ipso and 2-C of *p*-Tol	4-Me of *p*-Tol
4a[b]	93.2	234.3, 228.5	156.9	104.3, 85.2	21.5
6a[e]	94.4	233.7, 230.3	144.3	105.8, 86.5	21.6
16c[e]	94.0	238.6, 232.3	162.5	102.8, 90.2	21.5
17[e]	94.5	237.6, 231.8	159.0	105.7, 85.8	21.4
18[e]	93.0	220.0, 213.9	159.7	101.7, 75.9	21.4
20a[b]	94.3	231.2, 226.5	155.7 or 144.9	104.0, 83.7	21.5
21a[b]	94.1	236.2, 227.8	166.1 or 153.5	102.9, 87.0	21.4
22a[b]	94.1	234.4, 228.8	161.7	103.0, 89.3	21.3

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] Doublets with $^3J_{HH}$ = 8–9 Hz, often only partially visible. [d] Not visible. [e] In CD_2Cl_2.

Spectral Data. The spectral data of the bimetallic products indicate that all these complexes must be closely related to each other. It is therefore not desirable to discuss the spectral data of each individual complex. Nor is it helpful to compare the spectral data of the complexes **4** and **6–9**, which are rather similar. It is more important to compare the spectral data for a selected number of μ-alkylidene complexes, one example for each different cyclopalladated ligand (Table 2). Between these products, the greatest variation in structure can be expected. All complexes listed in Table 2 have in common the $Cp(CO)_2MC(4\text{-}Tol)$ fragment; therefore, the following discussion will be limited to the spectral features of this fragment.

$Cp(CO)_2M$ Fragment. The cyclopentadienyl ligand displays a constant signal in the carbon NMR spectra at 93 or 94 ppm and a characteristic singlet in the proton NMR spectra at 4.75–4.45 ppm; i.e., it has been shielded by 1 ppm as compared in the corresponding metallacarbynes (**3a**, 5.52 ppm; **3b**, 5.67 ppm). In the infrared spectra, two stretching frequencies appear in the carbonyl region, one terminal (μ_1) above 1960 cm^{-1} and one semibridging (μ_2) at 1850–1810 cm^{-1}.[19] This is in agreement with the structure of **22b**. The carbonyl carbons usually give two signals in the carbon NMR spectra at 220–215 ppm, which implies that they do not exchange on the carbon NMR time scale.

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(15) See, for example: Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G.; Bembenek, E. *Organometallics* **1994**, *13*, 1243.

(16) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 642.

(17) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1593.

(18) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

(19) Elschenbroich, C.; Salzer, A. *Organometallics*; VCH Verlagsgesellschaft: Weinheim, Germany, 1986; p 220.

The Bridging Carbon C_3. In the carbon NMR spectra of compound **4e**, one signal was found at 155.1 ppm with a strong coupling constant (56.4 Hz) with the phosphorus atom of the PMe_2Ph ligand, which we assigned to the central carbon C_3 bridging the tungsten and the palladium atoms. Also for compound **7c** inverse long-range correlation spectra[20] allowed us to unambiguously assign a resonance at 147.7 ppm to this carbon. For the other compounds of the series, although we did not perform the complete procedure for the assignment, we could always find one resonance in the 160–140 ppm region which we tentatively assigned to this carbon atom. The chemical shift of this carbon atom is within the accepted range predicted for μ-alkylidene complexes (100–200 ppm).[18]

***p*-Tolyl Group.** The aromatic protons of the *p*-tolyl group are partially visible in the proton NMR spectra, due to frequent overlap with the aromatic protons of the cyclopalladated ligand. They always appear as doublets corresponding to one proton ($^3J_{HH}$ = 8–9 Hz), as expected for an AA′BB′ pattern. The COSY $^1H-^{13}C$ spectrum of complex **9** allows for an unambiguous assignment of the tolyl protons to the signals δ 7.27 (m, 2 H), 7.07, and 6.70 (AB, 2 H, $^3J_{HH}$ = 9 Hz) (CD_2Cl_2). It clearly shows the AA′BB′ pattern due to the inequivalence of all four tolyl protons.

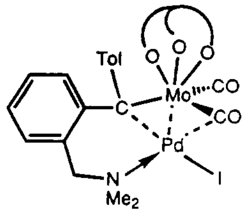
In the carbon NMR spectra of the μ-alkylidene complexes, two remarkable signals are present in the region 100–80 ppm. They were shown by various NMR analyses[20] to be the ipso and the ortho carbon atoms, respectively, of the *p*-tolyl group. A rational explanation for this unusual high-field chemical shift (which is likely to be due to an η^2 interaction of the aryl ring with the Mo or W atom) is beyond the scope of the present paper and it will thus be analyzed in detail elsewhere.[20]

Discussion

Structure and Bonding. The μ-alkylidene complexes all share a fragment derived from a metallacarbyne, and the characteristic spectral data of this fragment confirm that the structures of these complexes are closely related. This is quite remarkable, since important differences in the groups around the bimetallic unit exist between these molecules. Apparently, the metallacarbyne and the palladium fragments are locked together in a geometry which is insensitive to changes in the cyclopalladated ligands. Even the nature of the six-electron ligand on the carbyne metal is relatively unimportant, as is clear from the crystal structures of complexes **22b** and **23**.[21] The geometries around palladium and the carbyne metal are almost identical in both cases, while the ligand properties of the cyclopentadienyl anion and the tripod ligand in **23** are rather different. It appears therefore that, by variation of the parameters discussed, a great number of these μ-alkylidene complexes may be obtained.

Since the bimetallic complexes are formally built up from the metallacarbyne $Cp(CO)_2M{\equiv}CR$ (18 valence electrons) and the unsaturated monomer Pd(C–Y)X (14 valence electrons), the molecule is short of 2 electrons (34 valence electrons required). The distribution of the electrons between the metal M and palladium will determine which metal is the most unsaturated. From the structural and spectral data, it can be inferred that the bimetallic products are μ-alkylidene complexes[18] with a metal–metal interaction. They can thus be drawn either as dimetallacyclopropanes (**a**) or as a metallacarbene bridging a Pd(II) center (**b**) (Chart 8; C–Y represents the cyclopalladated ligand).

Chart 7



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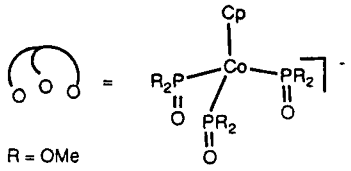
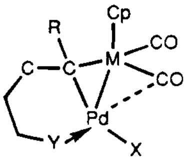
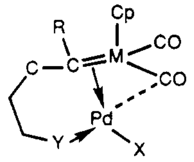


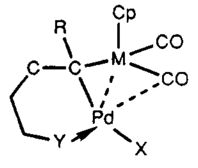
Chart 8



a



b



c

The comparison with reported dimetallcyclopropanes[17] reveals that our bimetallic complexes form a novel class within the family of μ-alkylidenes. The chemical shift of their bridging carbon μ-C indicates some contribution of sp^2 hybridization in this carbon. In a limiting case, however, both the M–μ-C and Pd–μ-C bonds can be considered as covalent single bonds, which defines the complex as being intermediate between a μ-alkylidene and a dimetallaalkyl complex (**c**; Chart 8).

This description is supported by the geometry around palladium, in which μ-C, Y, and X provide four electrons to the metal. The missing two electrons seem to be provided by the M–C–O unit, which suggests that the metal M is more unsaturated than the Pd center.

Analogies between Alkynes and Metallacarbynes. All cyclopalladated complexes of the ligands dmba (**1**), bms (**2**), 8mquin (**10**), bhq (**11**), 8equin (**12**), bzpy (**13**), bpdma (**14**), and bpms (**15**) are able to undergo carbon–carbon coupling reactions with both the metallacarbynes $Cp(CO)_2M{\equiv}CR$ (**3**) and disubstituted

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[20] Macchioni, A.; Pregosin, P. S.; Engel, P. F.; Pfeffer, M.; Daran, J. C.; Vaissermann, J. To be submitted for publication.

[21] Kläui, W.; Hamers, H.; Pfeffer, M.; De Cian, A.; Fischer, J. *J. Organomet. Chem.* **1990**, *394*, 213.

alkynes. The product results in both cases from the cleavage of the palladium−carbon bond, followed by the formation of a new carbon−carbon bond between the cyclopalladated ligand and an sp carbon. The important number of products obtained from metallacarbynes in this way confirms that a strong analogy exists between internal alkynes and these metallacarbynes, although a few differences must be taken into account.

In the reaction of cyclopalladated complexes with metallacarbynes, important differences in the total reaction time exist between the various cyclopalladated ligands. For example, the dmba complex **1a** reacts readily with the molybdenum metallacarbyne **3a** to afford a μ-alkylidene, whereas the analogous chloride complexes of 8equin and bhq do not undergo a C−C coupling reaction at all. This important difference has also been observed in the insertion reaction with internal alkynes.

In contrast, the bms complex **2** reacts much faster with the metallacarbynes **3** than the corresponding dmba complex **1a**, while the opposite has been observed for internal alkynes. Isocyanides are also known to insert into the Pd−C bond of the dmba and bms complexes, and in this case, the bms complex is much more reactive than its dmba analogue.[22] We have no rational explanation for this apparent similar behavior of metallacarbynes and isocyanides.

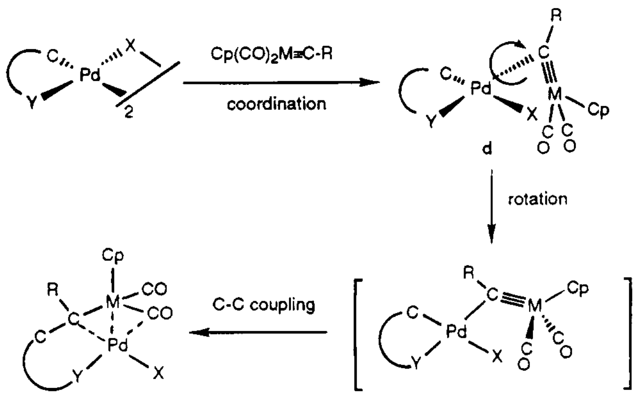
A detailed comparison of the total reaction time for each of the cyclopalladated ligands is desirable, but no data are available yet for any of these reactions.

Pathway of μ-Alkylidene Formation. The carbon−carbon coupling reaction between metallacarbynes and cyclopalladated ligands is a novel reaction, and no kinetic data are available to support a proposed mechanism. However, since the analogy between metallacarbynes and internal alkynes holds for a number of examples, it is reasonable to suggest that the mechanisms of their C−C coupling reactions with cyclopalladated ligands will be similar. In a simplified picture, a metallacarbyne may be considered as a polarized alkyne, in which one of the substituents is a strong electron-attracting group.

On the basis of studies by Maitlis,[23] Huggins,[24] and Samsel,[25] a generally accepted mechanism for the insertion of alkynes into a Pd−C bond has been proposed.[4] It is believed that, in a first step, the alkyne displaces a chloride bridge to form a coordination complex. One dimeric alkyne coordination complex has been isolated, but no X-ray structure is available.[26] In a second step, a rotation around the coordination bond brings the alkyne into the palladium plane, with the carbon bearing the smallest substituent next to palladium. Finally, a migratory insertion of the alkyne unit into the palladated carbon then results in the formation of the carbon−carbon bond.

In several cases the formation of the μ-alkylidene complexes (i.e. compounds **6**, **7c**, **8a**,**b**, and **16**−**18**) is preceded by the formation of a highly colored transient species whose stability depends upon the nature of the cyclopalladated ligand. It is very likely that these species all share an analogous structure which is closely related to that of **19** (Chart 5). In these compounds the metallacarbyne unit is interacting with the palladium atom via its carbyne carbon only, and it may well represent the first interaction between the two organometallic species. This compound may be considered as an intermediate that precedes the actual insertion reaction into the Pd−C bond.[9b]

Scheme 1



Taking this into account, a pathway can be proposed for the formation of μ-alkylidenes (Scheme 1). The carbyne carbon in complex **d** is coordinated exactly at the fourth coordination site, trans to the donor atom Y. When another donor ligand such as pyridine is present, no such complex can be formed, and this demonstrates the importance of an easily substituted ligand on the palladium center.

In **d**, the carbyne carbon is already in a position cis to the palladated carbon, whereas the M≡C bond is perpendicular to the coordination plane of Pd. The next step should thus involve the rotation of the metallacarbyne ligand around the Pd−C coordination bond so that the M≡C bond is now coplanar to the Pd plane. It cannot be excluded that the halogen group X is decoordinated before or during the rotation to form the cationic species $[Pd(C-Y)(\eta^2\text{-}Cp(CO)_2M{\equiv}CR)]^+$. This would liberate some space in the plane around palladium, which might facilitate the rotation of the triple bond. After the C−C coupling reaction, the halogenide anion could be coordinated again to form a neutral bimetallic complex. When the M≡C bond is positioned in the plane of the palladium, the carbon−carbon bond can be formed via the migration of the carbyne carbon onto the palladated carbon or vice versa.

Concluding Remarks

We have shown that the metallacarbynes $Cp(CO)_2M{\equiv}CR$ (M = Mo, W; R = 4-Tol, 4-$C_6H_4Bu^t$, 2,6-$C_6H_3Me_2$, cyclo-1-C_5H_7) may formally insert into the palladium−carbon bond of a series of cyclopalladated ligands (dmba, 4-F-dmba, 4,5-OCH_2O-dmba, bms, 8mquin, bhq, 8equin, bzpy, bpdma, and bpms). All these complexes are known to undergo similar insertion reactions with disubstituted alkynes. This demonstrates for the first time the general application of the isolobal analogy between alkynes and metallacarbynes in the synthesis of new carbon−carbon bonds.

It has become clear that the nature of the cyclopalladated ligand greatly influences the kinetics of the

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[22] Dupont, J.; Pfeffer, M.; Daran, J. C.; Jeanin, Y. *Organometallics* **1987**, *6*, 899.

[23] (a) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93. (b) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161.

[24] Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

[25] Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.

[26] Hosokawa, T.; Moritani, I.; Nishioka, S. *Tetrahedron Lett.* **1969**, 3833.

coupling reaction, as was observed for the insertion of alkynes. In virtually all cases, μ-alkylidene complexes can be obtained, but the total reaction time and the selectivity of the reaction varies strongly with the ligand. In contrast, changes in the nature of the halogen bridge, the carbyne metal, or the carbyne substituent seem relatively unimportant compared to changes in the nature of the cyclopalladated ligand.

The bimetallic complexes obtained in the reaction with these metallacarbynes can be considered as μ-alkylidene complexes with a relatively weak metal–metal bond. They all share the same geometry around the palladium atom, which is highly surprising. It suggests that they form a well-defined novel class of complexes that has potential in being extended to a great number of examples.

Experimental Section

General Considerations. All reactions were performed under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried on sodium (diethyl ether, hexane) or calcium dihydride (dichloromethane) prior to use. Except when specified otherwise, NMR spectra were recorded on either a Bruker WP 200 SY spectrometer (200 MHz, ∂ in ppm referenced to internal TMS, *J* in Hz) or a Bruker AC 300 spectrometer (300 MHz); 400 MHz NMR spectra were provided by the Service RMN de la Faculté de Chimie de Strasbourg, and the infrared spectra were recorded on a Bruker IFS 66 spectrometer (in CH_2Cl_2; ν in cm^{-1}). Microanalyses were carried out by the Service de Microanalyse du CNRS in Strasbourg.

The metallacarbynes $Cp(CO)_2Mo{\equiv}C$-4-Tol (**3a**), $Cp(CO)_2W{\equiv}C$-4-Tol (**3b**), $Cp(CO)_2W{\equiv}C$-4-$C_6H_4Bu^t$ (**3c**), $Cp(CO)_2W{\equiv}C$-2,6-$C_6H_3Me_2$ (**3d**), and $Cp(CO)_2W{\equiv}C$-cyclo-1-C_5H_7 (**3e**) were prepared according to a general method[27] in yields above 60% (except for **3e**). The cyclopalladated complexes have been prepared according to literature procedures: $[Pd(dmba)Cl]_2$ (**1a**),[28] $[Pd(bms)Cl]_2$ (**2**),[32] $[Pd(8mquin)Cl]_2$ (**10a**),[28,29] $[Pd(8equin)I]_2$ (**12**),[11] $[Pd(bhq)I]_2$ (**11**),[30] $[Pd(bzpy)Cl]_2$ (**13a**),[31] $[Pd(bpdma)Cl]_2$ (**14**),[13] and $[Pd(bpms)Cl]_2$ (**15**).[32] The dmba derivatives $[Pd(4\text{-F-dmba})Cl]_2$ (**1c**) and $[Pd(4,5\text{-}OCH_2O\text{-dmba})Cl]_2$ (**1d**) have been prepared according to the same method as that reported for the dmba complex **1a**. The iodide analogues of the cyclopalladated complexes have been prepared from the corresponding chloride complexes via an exchange reaction in acetone.[6]

Syntheses. [Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(dmba)][Pd(Cl)] (4a). To a stirred solution of $[Pd(dmba)Cl]_2$ (**1a**; 1.144 g, 2.07 mmol) in dichloromethane (30 mL) was added $Cp(CO)_2Mo{\equiv}C$-4-Tol (**3a**; 1.420 g, 4.43 mmol), and the color changed to deep red. After 1.5 h, the color had turned to a lighter red and the solution was concentrated *in vacuo* to saturation (about 10 mL). An excess of hexane (70 mL) was added, and the orange precipitate was filtered off on a glass filter. Washing the solid with diethyl ether (5 mL) and drying *in vacuo* gave **4a** as an orange powder (2.238 g, 93%). Anal. Calcd for $C_{24}H_{24}ClMoNO_2Pd$ (M_r = 596.28): C, 48.35; H, 4.06; N, 2.35. Found: C, 47.65; H, 4.02; N, 2.26. ^1H NMR ($CDCl_3$): ∂ 7.46–7.27 (m, 5 H arom), 7.11–7.01 (m, 2 H arom), 6.74 (d, 1 H arom, $^3J_{HH}$ = 8.7), 4.63 (s, 5 H, Cp), 3.27, 2.95 (AB pattern, 2 H, NCH_2, $^2J_{HH}$ = 11.5), 2.52, 2.41 (2 s, 6 H, NMe_2), 2.32 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): ∂ 234.3, 228.5 (CO), 156.9 (μ-C), 145.9, 138.8, 135.3, 132.9, 131.1, 130.9, 129.6, 127.9, 127.8, 126.5 (C arom), 104.3 (C ipso of 4-Tol), 93.2 (Cp), 85.2 (2-C of 4-Tol), 68.1 (NCH_2), 51.1, 47.5 (NMe_2), 21.5 (4-Me). IR ν_{CO}: 1975, 1829.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(dmba)][Pd(I)] (4b). This complex was prepared by following the same procedure as for **4a**, starting from $[Pd(dmba)I]_2$ (**1b**) and $Cp(CO)_2Mo{\equiv}C$-4-Tol (**3a**): total reaction time 30 min; orange powder (85%). Anal. Calcd for $C_{24}H_{24}IMoNO_2Pd$ (M_r = 687.73): C, 41.92; H, 3.52; N, 2.04. Found: C, 42.05; H, 3.58; N, 2.06. ^1H NMR ($CDCl_3$): ∂ 7.45–7.29 (m, 5 H arom), 7.12–7.05 (m, 2 H arom), 6.72 (d, 1 H arom, $^3J_{HH}$ = 7.8), 4.63 (s, 5 H, Cp), 3.28, 2.97 (AB pattern, 2 H, $^2J_{HH}$ = 11.4), 2.58, 2.45 (2 s, 6 H, NMe_2), 2.33 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): ∂ 233.9, 229.0 (CO), 159.0 (μ-C), 145.5, 138.8, 135.4, 133.2, 131.2, 130.9, 129.8, 128.1, 127.9, 126.6 (C arom), 103.7 (C ipso of 4-Tol), 93.4 (Cp), 84.2 (2-C of 4-Tol), 67.9 (NCH_2), 52.6, 49.7 (NMe_2), 21.5 (4-Me). IR ν_{CO}: 1980, 1830.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(dmba)][Pd(Cl)] (4c). This complex was prepared by following the same procedure as for **4a**, starting from $[Pd(dmba)Cl]_2$ (**1a**) and $Cp(CO)_2W{\equiv}C$-4-Tol (**3b**): total reaction time 2 h; orange powder (93%). Anal. Calcd for $C_{24}H_{24}ClNO_2PdW$ (M_r = 684.19): C, 42.13; H, 3.54; N, 2.05. Found: C, 41.78; H, 3.53; N, 1.99. ^1H NMR ($CDCl_3$): ∂ 7.49–7.28 (m, 4 H arom), 7.14 (d, 1 H arom, $^3J_{HH}$ = 6.7), 7.06 (d, 1 H arom, $^3J_{HH}$ = 7.1), 6.95 (d, 1 H arom, $^3J_{HH}$ = 8.8), 6.73 (d, 1 H arom, $^3J_{HH}$ = 8.8), 4.71 (s, 5 H, Cp), 3.29, 3.11 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 11.5), 2.52, 2.38 (s, 6 H, NMe_2), 2.32 (s, 3 H, 4-Me). ^{13}C NMR (CD_2Cl_2): ∂ 216.6 (CO), 146.8 (μ-C), 141.7, 138.1, 137.0, 134.3, 132.2, 131.0, 129.8, 128.6, 127.3, 126.7 (C arom), 102.2 (C ipso of 4-Tol), 92.2 (Cp), 77.3 (2-C of 4-Tol), 68.4 (CH_2), 50.9, 47.1 (NMe_2), 21.2 (4-Me). IR ν_{CO}: 1964, 1827.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(dmba)][Pd(I)] (4d). This complex was prepared by following the same procedure as for **4a**, starting from $[Pd(dmba)I]_2$ (**1b**) and $Cp(CO)_2W{\equiv}C$-4-Tol (**3b**): total reaction time 30 min; orange powder (93%). Anal. Calcd for $C_{24}H_{24}INO_2PdW$ (M_r 775.64): C, 37.17; H, 3.12; N, 1.81. Found: C, 37.06; H, 3.11; N, 1.81. ^1H NMR ($CDCl_3$): ∂ 7.50–7.29 (m, 4 H arom), 7.16 (d, 1 H arom, $^3J_{HH}$ = 6.4), 7.06 (d, 1 H arom, $^3J_{HH}$ = 7), 6.98 (d, 1 H arom, $^3J_{HH}$ = 8.8), 6.71 (d, 1 H arom, $^3J_{HH}$ = 8.8), 4.71 (s, 5 H, Cp), 3.33, 3.14 (AB pattern, 2 H, $^2J_{HH}$ = 11.5), 2.58 (s, 3 H, NMe), 2.43 (s, 3 H, NMe), 2.33 (s, 3 H, 4-Me). ^{13}C NMR ($CDCl_3$): ∂ 221.3, 215.2 (CO), 145.9 (μ-C), 145.6, 137.6, 136.8, 134.1, 132.0, 130.8, 129.7, 128.3, 127.4, 126.6 (C arom), 101.3 (C ipso of 4-Tol), 91.7 (Cp), 77.2 (2-C of 4-Tol), 68.1 (CH_2), 52.5, 49.5 (NMe_2), 21.3 (4-Me). IR ν_{CO}: 1969, 1830.

{[Cp(CO)(μ-CO)W][μ-C(4-Tol)(dmba)][Pd(PMe_2Ph)]}BF_4 (4e). To a stirred solution of $[Pd(dmba)Cl]_2$

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(**1a**; 351 mg, 0.64 mmol) in dichloromethane (30 mL) was added a solution of $AgBF_4$ (272 mg, 1.40 mmol) and acetonitrile (0.04 mL, 1.42 mmol) in dichloromethane (10 mL). After the mixture was stirred for 5 min, the precipitate was filtered off on a Celite pad, and $Cp(CO)_2W{\equiv}C$-4-Tol (**3b**; 556 mg, 1.36 mmol) was added to the filtrate. After this mixture was stirred for 1 h, a 0.05 M solution of PMe_2Ph (27 mL, 1.35 mmol) in dichloromethane was added and the solution was concentrated *in vacuo* to saturation. An excess of hexane (40 mL) was added, and the precipitate was filtered off, washed twice with ether (2 × 15 mL), and dried *in vacuo* to give an orange-brown powder (1.024 g, 96%). Anal. Calcd for $C_{32}H_{35}BF_4NO_2PPdW$ (M_r = 873.71): C, 43.99; H, 4.05; N, 1.60. Found: C, 44.4; H, 4.5; N, 1.7. ^1H NMR ($CDCl_3$): ∂ 7.59–7.11 (m, 12 H arom), 6.70 (d, 1 H arom, $^3J_{HH}$ = 8.8), 4.89 (s, 5 H, Cp), 3.27 3.01 (AB pattern, 2 H, $^2J_{HH}$ = 11.6, NCH_2), 2.41 (s, 3 H, Me), 2.02 (s, 3 H, Me), 1.86 (s, 3 H, Me), 1.73 (d, 3 H, $^2J_{PH}$ = 6.8, PMe), 1.58 (d, 3 H, $^2J_{PH}$ = 7.0, PMe). ^{13}C NMR ($CDCl_3$): ∂ 223.3 (J_{PC} = 4.2), 215.8 (J_{PC} = 4.5) (CO), 155.2 (μ-C, $^2J_{PC}$ = 56.4), 146.0, 140.6, 135.8, 135.0, 131.6, 130.7, 130.3, 130.1, 129.5, 129.3, 128.0, 127.5 (C arom), 100.2 (C ipso of 4-Tol), 93.1 (Cp), 79.0 (2-C of 4-Tol), 69.4 (NCH_2), 52.4, 49.6 (NMe_2), 21.4 (4-Me), 13.9, 13.2 (PMe_2, $^1J_{PC}$ = 21). IR ν_{CO}: 1974, 1832.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bms)][Pd(Cl)] (6a). To a stirred solution of $[Pd(bms)Cl]_2$ (**2**; 366 mg, 0.66 mmol) in dichloromethane (20 mL) was added $Cp(CO)_2Mo{\equiv}C$-4-Tol (**3a**; 457 mg, 1.43 mmol), whereupon the color changed instantaneously to deep red-brown. Over 2 min, a red-orange suspension formed, and after 30 min, the solvent was removed *in vacuo*. The residue was washed with diethyl ether (2 × 15 mL) and dried *in vacuo*. Complex **6a** was obtained as a red-orange powder (592 mg, 75%). Anal. Calcd for $C_{23}H_{21}ClMoO_2PdS$ (M_r = 599.29) (+0.25CH_2Cl_2): C, 45.00; H, 3.50; S, 5.17. Found: C, 44.8; H, 3.4; S, 5.2. ^1H NMR ($CDCl_3$): ∂ 7.41–7.37 (m, 1 H arom), 7.25 (m, 3 H arom), 7.16 (d, 1 H arom, $^3J_{HH}$ = 7.5), 7.07 (d, 1 H arom, $^3J_{HH}$ = 9.1), 6.86 (d, 1 H arom, $^3J_{HH}$ = 6.3), 6.71 (d, 1 H arom, $^3J_{HH}$ = 9.4), 4.65 (s, 5 H, Cp), 3.45, 3.11 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 13.1), 2.34 (s, 3 H, 4-Me), 2.29 (s, 3 H, SMe). ^{13}C NMR (400 MHz, CD_2Cl_2, +Cr(acac)): ∂ 233.7, 230.3 (CO), 144.3 (μ-C), 139.6, 136.7, 133.6, 131.8, 131.1, 130.8, 129.6, 127.8, 127.0 (C arom), 105.8 (C ipso of 4-Tol), 94.4 (Cp), 86.5 (2-C of 4-Tol), 40.0 (CH_2), 21.6 (4-Me), 18.8 (SMe). IR ν_{CO}: 1975, 1839.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(bms)][Pd(Cl)] (6b). This complex was prepared by following the same procedure as for **6a**, starting from $[Pd(bms)Cl]_2$ (**2**) and $Cp(CO)_2W{\equiv}C$-4-Tol (**3b**): total reaction time 1 h; fine red powder (87%). Anal. Calcd for $C_{23}H_{21}ClO_2PdSW$ (M_r = 687.20) (+0.5 CH_2Cl_2): C, 38.68; H, 3.04; S, 4.61. Found: C, 38.10; H, 3.00; S, 4.14. ^1H NMR ($CDCl_3$): ∂ 7.42–7.36 (m, 1 H arom), 7.27 (m, 2 H arom), 7.14 (d, 2 H arom, $^3J_{HH}$ = 7.4), 7.04–6.97 (m, 2 H arom), 6.70 (d, 1 H arom, $^3J_{HH}$ = 8.6), 4.74 (s, 5 H, Cp), 3.64, 3.13 (AB pattern, 2 H, SCH_2, $^2J_{HH}$ = 13.1), 2.33 (s, 3 H, Me), 2.27 (s, 3 H, Me). ^{13}C NMR (400 MHz, $CDCl_3$): ∂ 220.0, 214.9 (CO), 144.3 (μ-C), 137.8, 134.2, 132.3, 131.2, 130.4, 129.3, 126.8, 126.6 (C arom), 103.2 (C ipso of 4-Tol), 92.1 (Cp), 77.7 (2-C of 4-Tol), 39.7 (CMe), 21.3 (4-Me), 18.7 (SMe). IR ν_{CO}: 1967, 1837.

[Cp(CO)(μ-CO)W][μ-C(4-$C_6H_4Bu^t$)(dmba)]-[Pd(I)] (7a). To a stirred solution of $[Pd(dmba)I]_2$ (**1b**; 331 mg, 0.45 mmol) in dichloromethane (20 mL) was added $Cp(CO)_2W{\equiv}C$-4-$C_6H_4Bu^t$ (**3c**; 434 mg, 0.96 mmol). After 45 min, the solution was concentrated *in vacuo* to saturation and an excess of hexane (30 mL) was added. The precipitate was filtered off, washed with hexane (10 mL), and dried *in vacuo*. Complex **7a** was obtained as an orange powder (665 mg, 90%). Anal. Calcd for $C_{27}H_{30}INO_2PdW$ (M_r = 817.73): C, 39.65; H, 3.71; N, 1.71. Found: C, 39.59; H, 3.45; N, 1.69. ^1H NMR ($CDCl_3$): ∂ 7.49–7.40 (m, 2 H arom), 7.32–7.18 (m, 4 H arom), 7.07 (d, 1 H arom, $^3J_{HH}$ = 7), 6.75 (d, 1 H arom, $^3J_{HH}$ = 9), 4.68 (s, 5 H, Cp), 3.38, 3.15 (AB pattern, 2 H, NCH_2, $^2J_{HH}$ = 11), 2.60, 2.44 (2 s, 6 H, NMe_2), 1.29 (s, 9 H, CMe_3). ^{13}C NMR ($CDCl_3$): ∂ 221.5, 215.4 (CO), 150.7, 145.8 (μ-C), 136.8, 130.9, 129.8, 128.4, 127.8, 127.2, 127.6, (C arom), 101.4 (C ipso of 4-C_6H_4-Bu^t), 91.8 (Cp), 74.7 (2-C of 4-$C_6H_4Bu^t$), 68.2 (NCH_2), 52.6, 49.5 (NMe_2), 35.1 (*C*Me_3), 30.9 (3 C, C*Me*$_3$). IR ν_{CO}: 1969, 1830.

[Cp(CO)(μ-CO)W][μ-C(2,6-$C_6H_3Me_2$)(bms)]-[Pd(Cl)] (7b). To a stirred solution of $[Pd(bms)Cl]_2$ (**2**; 305 mg, 0.55 mmol) in dichloromethane (30 mL) was added $Cp(CO)_2W{\equiv}C$-2,6-$C_6H_3Me_2$ (**3d**; 488 mg, 1.16 mmol). After 16 h, the deep red mixture was filtered over a glass filter and the fitrate was concentrated *in vacuo* to saturation. An excess of hexane (50 mL) was added. The precipitate was filtered off, washed with hexane (20 mL), and dried *in vacuo*. Complex **7b** was obtained as an orange powder (608 mg, 79%). Anal. Calcd for $C_{24}H_{23}ClO_2PdSW$ (M_r = 701.23) (+0.5CH_2Cl_2): C, 39.57; H, 3.26. Found: C, 39.89; H, 3.10. ^1H NMR ($CDCl_3$): ∂ 7.33–7.16 (m, 5 H arom), 6.68–6.52 (m, 2 H arom), 4.71 (s, 5 H, Cp), 3.64, 3.39 (AB pattern, 2 H, SCH_2, $^2J_{HH}$ = 12.6), 3.20, 1.64 (2 s, 6 H, $ArMe_2$), 2.23 (s, 3 H, SMe). ^{13}C NMR ($CDCl_3$): ∂ 214.8 (CO), 154.8 (μ-C), 145.9, 141.3, 139.9, 136.6, 131.9, 129.1, 129.0, 125.9, 120.8 (C arom), 100.4 (C ipso of 2,6-C_6H_3-Me_2), 94.1 (Cp), 83.7 (2-C of 2,6-$C_6H_3Me_2$), 38.9, 32.4, 24.0, 18.2 (SCH_2, SMe, $ArMe_2$). IR ν_{CO}: 1965, 1833.

[Cp(CO)(μ-CO)W][μ-C(1-cyclo-C_5H_7)(dmba)]-[Pd(Cl)] (7c). To a stirred solution of $[Pd(dmba)Cl]_2$ (**1a**; 257 mg, 0.47 mmol) in dichloromethane (15 mL) was added $Cp(CO)_2W{\equiv}C$-1-cyclo-C_5H_7 (**3e**; 385 mg, 1.00 mmol), and the color changed to deep red-brown. After 30 min, the orange solution was concentrated *in vacuo* to 5 mL. An excess of hexane (40 mL) was added, and the precipitate was filtered off. Washing with hexane (25 mL) and drying *in vacuo* gave **7c** as a bright yellow powder (531 mg, 87%). Anal. Calcd for $C_{22}H_{24}ClNO_2PdW$ (M_r = 660.17) (+0.5CH_2Cl_2): C, 38.46; H, 3.59; N, 1.99. Found: C, 38.14; H, 3.50; N, 1.89. ^1H NMR ($CDCl_3$): ∂ 7.33–7.22 (m, 3 H, dmba), 6.85 (d, 1 H, $^3J_{HH}$ = 7.2, dmba), 5.34 (s, 5 H, Cp), 5.26 (d, 1 H, $^3J_{HH}$ = 5.0, 2-H of C_5H_7), 3.66, 3.27 (AB pattern, 2 H, NCH_2, $^2J_{HH}$ = 11.4), 3.12–2.93 (m, 2 H, C_5H_7), 2.69, 2.38 (2 s, 6 H, NMe_2), 2.31–1.96 (m, 2 H, C_5H_7), 1.32–1.25 (m, 2 H, C_5H_7). ^{13}C NMR ($CDCl_3$): ∂ 221.5, 212.4 (CO), 147.7 (μ-C), 145.3, 134.9, 130.0, 129.5, 126.2 (C arom), 109.7 (C ipso of C_5H_7), 90.7 (Cp), 68.4 (NCH_2), 51.0 and 47.0 (NMe_2), 61.1, 33.0, 31.6, 21.9 (C_5H_7). IR ν_{CO}: 1967, 1816.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(4-F-dmba)]-[Pd(Cl)] (8a). To a stirred solution of $[Pd(4\text{-}F\text{-}dmba)Cl]_2$ (**1c**; 240 mg, 0.41 mmol) in dichloromethane (15 mL) was added Cp(CO)$_2$Mo≡C-4-Tol (**3a**; 274 mg, 0.86 mmol), and the color changed immediately to deep red-brown. Over 2 h, a red solution formed, which was concentrated *in vacuo* to 5 mL. After hexane was added (40 mL), a solid was filtered off. Washing the solid with hexane (10 mL) and drying *in vacuo* gave **8a** as a red powder (410 mg, 81%). Anal. Calcd for $C_{24}H_{23}ClFMoNO_2Pd$ (M_r = 614.27) (+0.25CH_2Cl_2): C, 45.40; H, 3.73; N, 2.20. Found: C, 45.76; H, 3.49; N, 2.23. ^{1}H NMR ($CDCl_3$): ∂ 7.30−7.23 (m, 3 H arom), 7.10−6.95 (m, 2 H arom), 6.82−6.74 (m, 2 H arom), 4.64 (s, 5 H, Cp), 3.19, 2.96 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 11.6), 2.53, 2.43, 2.34 (3 s, 9 H, 4-Me and NMe_2). ^{13}C NMR ($CDCl_3$): ∂ 233.5, 228.7 (CO), 163.2 (d, $^1J_{CF}$ = 249.4, 4-C of 4-F-dmba), 154.1 (μ-C), 148.3 (d, $^3J_{CF}$ = 8.6, 2-C of 4-F-dmba), 138.9 (4-Tol), 133.1 (4-Tol), 132.4 (d, $^3J_{CF}$ = 8.6, 6-C of 4-F-dmba), 131.4 and 127.6 (4-Tol), 114.8 (d, J_{CF} = 21.9, 4-F-dmba), 112.7 (d, J_{CF} = 21.3, 4-F-dmba), 104.4 (C ipso of 4-Tol), 93.3 (Cp), 85.1 (2-C of 4-Tol), 67.3 (CH_2), 51.1, 47.4 (NMe_2), 21.5 (4-Me). IR ν_{CO}: 1977, 1831.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(4-F-dmba)][Pd(Cl)] (8b). This complex was prepared by following the same procedure as for **8a**, starting from [Pd(4-F-dmba)Cl]$_2$ (**1c**) and Cp(CO)$_2$W≡C-4-Tol (**3b**): total reaction time 2 h; red powder (90%). Anal. Calcd for $C_{24}H_{23}ClFNO_2PdW$ (M_r = 702.18) (+0.5CH_2Cl_2): C, 39.52; H, 3.26; N, 1.88. Found: C, 39.98; H, 3.31; N, 2.06. ^{1}H NMR ($CDCl_3$): ∂ 7.47 (d, 1 H arom, $^3J_{HH}$ = 6.3), 7.31−7.24 (m, 1 H arom), 7.15 (d, 1 H arom, $^3J_{HH}$ = 6.4), 7.02−6.97 (m, 2 H arom), 6.79−6.73 (m, 2 H arom), 4.72 (s, 5 H, Cp), 3.24, 3.12 (AB pattern, 2 H, NCH_2, $^2J_{HH}$ = 11.7), 2.53, 2.40, 2.34 (3 s, 9 H, 4-Me and NMe_2). ^{13}C NMR (400 MHz, CD_2Cl_2): ∂ 222.1, 216.7 (CO), 163.5 (d, $^1J_{CF}$ = 301.8, 4-C of 4-F-dmba), 148.8 (μ-C), 140.0 (4-F-dmba), 138.3 (4-Tol), 134.6, (4-Tol), 133.2 (4-F-dmba), 132.7 (d, $^3J_{CF}$ = 9, 4-F-dmba), 132.5 (4-Tol), 127.2 (4-Tol), 115.7 (d, $^2J_{CF}$ = 21.8, 4-F-dmba), 112.9 (d, $^2J_{CF}$ = 21.3, 4-F-dmba), 102.4 (C ipso of 4-Tol), 92.3 (Cp), 77.4 (2-C of 4-Tol), 67.7 (NCH_2), 51.0, 47.1 (NMe_2), 21.4 (4-Me). IR ν_{CO}: 1967, 1832.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(4,5-OCH$_2$O-dmba)][Pd(Cl)] (9). To a stirred suspension of [Pd(4,5-OCH$_2$O-dmba)Cl]$_2$ (**1d**; 252 mg, 0.39 mmol) in dichloromethane (30 mL) was added Cp(CO)$_2$Mo≡C-4-Tol (**3a**; 270 mg, 0.84 mmol). Over 30 min, the mixture became deep red-brown and the solution was concentrated *in vacuo* to 5 mL. An excess of hexane (80 mL) was added, and the precipitate was filtered off on a glass filter. Washing with hexane (20 mL) and drying *in vacuo* gave **9** as an orange-brown solid (395 mg, 79%). Anal. Calcd for $C_{25}H_{24}ClMoNO_4Pd$ (M_r = 640.29) (+CH_2Cl_2): C, 43.06; H, 3.62; N, 1.93. Found: C, 43.23; H, 3.56; N, 2.09. ^{1}H NMR ($CDCl_3$): ∂ 7.32−7.29 (m, 2 H, 4-Tol), 7.06, 6.79 (AB pattern, 2 H, $^2J_{HH}$ = 9.0, 4-Tol), 6.81 (s, 1 H arom), 6.60 (s, 1 H arom, OCH$_2$O-dmba), 6.07 (s, 2 H, OCH$_2$), 4.60 (s, 5 H, Cp), 3.15, 2.82 (AB pattern, 2 H, NCH_2, $^2J_{HH}$ = 11.6), 2.49, 2.42, 2.33 (3 s, 9 H, 4-Me and NMe_2). ^{13}C NMR ($CDCl_3$): ∂ 234.5, 229.2 (CO), 157.0 (μ-C), 148.3, 146.0, 140.2, 138.8 (C_{quat} arom), 133.0, 131.1 (CH, 4-Tol), 128.6 (C_{quat} arom), 127.8 (CH, 4-Tol), 111.2, 108.9 (C arom, OCH$_2$O-dmba), 104.4 (C ipso of 4-Tol), 101.6 (OCH$_2$), 93.3 (Cp), 85.3 (2-C of 4-Tol), 68.1 (CH_2), 50.8, 47.4 (NMe_2), 21.4 (4-Me). IR ν_{CO}: 1973, 1827.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(8mquin)][Pd(I)] (16a). This complex was prepared by following the same procedure as for **16c**, starting from [Pd(8mquin)I]$_2$ (**10b**) and Cp(CO)$_2$W≡C-4-Tol (**3b**): total reaction time 30 min; orange solid (59%). The solid obtained often contains impurities which are difficult to remove, due to the low solubility of **16a**. Anal. Calcd for $C_{25}H_{20}INO_2PdW$ (M_r = 783.62) (+0.5CH_2Cl_2): C, 37.07; H, 2.57; N, 1.70. Found: C, 37.33; H, 2.61; N, 1.66. ^{1}H NMR ($CDCl_3$): ∂ 10.04 (d, 1 H arom, $^3J_{HH}$ = 4.9), 8.21 (d, 1 H arom, $^3J_{HH}$ = 8.3), 7.84 (d, 1 H arom, $^3J_{HH}$ = 6.6), 7.72 (d, 1 H arom, $^3J_{HH}$ = 7.8), 7.54−7.00 (m, 6 H arom), 5.41, 4.27 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 16.5), 4.61 (s, 5 H, Cp), 2.24 (s, 3 H, 4-Me). ^{13}C NMR is not available due to the low solubility of the product: **16a** decomposed in CD_2Cl_2 during the measurement. IR ν_{CO}: 1965, 1819.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(8mquin)][Pd(Cl)] (16b). This complex was prepared by following the same procedure as for **16c**, starting from [Pd(8mquin)Cl]$_2$ (**10a**) and Cp(CO)$_2$Mo≡C-4-Tol (**3a**): total reaction time 2.5 h; orange powder (85%). Anal. Calcd for $C_{25}H_{20}ClMoNO_2Pd$ (M_r 604.26) (+0.5CH_2Cl_2): C, 47.36; H, 3.28; N, 2.17. Found: C, 47.18; H, 3.05; N, 2.09. ^{1}H NMR ($CDCl_3$): ∂ 9.92 (d, 1 H arom, $^3J_{HH}$ = 5.0), 8.20 (d, 1 H arom, $^3J_{HH}$ = 8.1), 7.82 (d, 1 H arom, $^3J_{HH}$ = 7.2), 7.72 (d, 1 H arom, $^3J_{HH}$ = 7.6), 7.53 (d, 1 H arom, $^3J_{HH}$ = 7.2), 7.47−7.33 (m, 2 H arom), 7.13−7.05 (m, 2 H arom), 6.95 (d, 1 H arom, $^3J_{HH}$ = 5.2), 5.44, 4.51 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 16.3), 4.62 (s, 5 H, Cp), 2.24 (s, 3 H, 4-Me). ^{13}C NMR (400 MHz, CD_2Cl_2): ∂ 234.3, 218.0 (CO), 156.5, 141.0 (μ-C), 140.0, 132.9, 131.5, 130.9, 128.9, 128.0, 126.9, 122.2 (C arom), 102.9 (C ipso of 4-Tol), 93.6 (Cp), 45.2 (CH_2), 21.6 (4-Me). IR ν_{CO}: 1972, 1811.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(8mquin)][Pd(I)] (16c). To a stirred suspension of [Pd(8mquin)I]$_2$ (**10b**; 394 mg, 0.53 mmol) in toluene (30 mL) was added Cp(CO)$_2$Mo≡C-4-Tol (**3a**; 358 mg, 1.12 mmol), and the color changed instantaneously to deep red-brown. After 45 min, the precipitate was filtered off from the orange-brown suspension and it was washed with hexane (20 mL). Drying *in vacuo* gave **16c** as an orange powder (602 mg, 82%). Anal. Calcd for $C_{25}H_{20}IMoNO_2Pd$ (M_r = 695.71): C, 43.16; H, 2.90; N, 2.01. Found: C, 43.40; H. 2.95; N, 1.89. ^{1}H NMR ($CDCl_3$): ∂ 10.09 (m, 1 H arom), 8.22 (d, 1 H arom, $^3J_{HH}$ = 8.1), 7.84 (d, 1 H arom, $^3J_{HH}$ = 7.1), 7.73 (d, 1 H arom, $^3J_{HH}$ = 7.3), 7.52 (m, 1 H arom), 7.39−7.01 (m, 5 H arom), 5.41, 4.34 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 16.2), 4.55 (s, 5 H, Cp), 2.23 (s, 3 H, 4-Me). ^{13}C NMR (400 MHz, CD_2Cl_2): ∂ 238.6, 232.3 (CO), 162.5 (μ-C), 160.2, 144.2, 140.4, 140.1, 140.1, 133.4, 131.7, 131.5, 130.7, 129.4, 129.0, 128.6, 127.3, 126.9, 122.2 (C arom), 102.8 (C ipso of 4-Tol), 94.0 (Cp), 90.2 (2-C of 4-Tol), 44.7 (CH_2), 21.5 (4-Me). IR ν_{CO}: 1972, 1812.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bhq)][Pd(I)] (17). To a stirred suspension of [Pd(bhq)I]$_2$ (**11**; 435 mg, 0.53 mmol) in dichloromethane (40 mL) was added Cp(CO)$_2$Mo≡C-4-Tol (**3a**; 367 mg, 1.15 mmol), and the color changed rapidly to deep red-brown. After 4 h, the suspension was concentrated *in vacuo* to 10 mL and hexane was added (20 mL). The precipitate was filtered off, washed with hexane (20 mL), and dried *in vacuo*. Complex **17** was obtained as a bright orange powder

(555 mg, 72%). Anal. Calcd for $C_{28}H_{20}IMoNO_2Pd$ (M_r = 731.74) (+0.25CH_2Cl_2): C, 45.06; H, 2.75; N, 1.86. Found: C, 44.90; H, 2.76; N, 1.86. ^{1}H NMR ($CDCl_3$): ∂ 9.45 (d, 1 H arom, $^3J_{HH}$ = 3.7), 8.18 (d, 1 H arom, $^3J_{HH}$ = 7.8), 7.92–7.61 (m, 4 H arom), 7.45–7.20 (m, 4 H arom), 6.85 (d, 1 H arom, $^3J_{HH}$ = 9.0), 6.47 (d, 1 H arom, $^3J_{HH}$ = 8.5), 4.73 (s, 5 H, Cp), 2.22 (s, 3 H, 4-Me). ^{13}C NMR (400 MHz, CD_2Cl_2): ∂ 237.6, 231.8 (CO), 159.0 (μ-C), 156.6, 139.1, 138.7, 135.9, 132.8, 131.4, 130.0, 129.3, 129.0, 128.5, 128.2, 128.1, 128.0, 126.9, 126.1, 122.6, 110.7 (C arom), 105.7 (C ipso of 4-Tol), 94.5 (Cp), 85.8 (2-C of 4-Tol), 21.4 (4-Me). IR ν_{CO}: 1973, 1822.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(8equin)][Pd(I)] (18). To a stirred suspension of [Pd(8equin)I]$_2$ (**12**; 388 mg, 0.51 mmol) in dichloromethane (80 mL) was added Cp(CO)$_2$Mo≡C-4-Tol (**3a**; 497 mg, 1.55 mmol), and the color changed immediately to deep red-brown. After 5.5 h, the mixture was filtered over a Celite pad, and when the solvent was evaporated from the solution, a brown oily solid was obtained. The residue was washed repeatedly with diethyl ether (6 × 15 mL) and then dried *in vacuo*. Complex **18** was obtained as a mustard yellow powder (150 mg, 21%). Anal. Calcd for $C_{26}H_{22}IMoNO_2Pd$ (M_r = 709.73) (+0.25CH_2Cl_2): C, 43.13; H, 3.11; N, 1.92. Found: C, 43.48; H, 2.88; N, 2.21. ^{1}H NMR ($CDCl_3$): ∂ 10.15 (d, 1 H arom, $^3J_{HH}$ = 3.4), 8.22 (d, 1 H arom, $^3J_{HH}$ = 8.2), 7.86 (d, 1 H arom, $^3J_{HH}$ = 7.1), 7.71 (d, 1 H arom, $^3J_{HH}$ = 6.7), 7.56–7.16 (m, 5 H arom), 7.07 (d, 1 H arom, $^3J_{HH}$ = 8.9), 4.56 (s, 5 H, Cp), 4.36 (q, 1 H, MeC*H*, $^3J_{HH}$ = 7.3), 2.22 (s, 3 H, 4-Me), 2.15 (d, 3 H, *Me*CH). ^{13}C NMR (400 MHz, CD_2Cl_2): ∂ 220.0, 213.9 (CO), 159.9 (μ-C), 156.8, 155.0, 145.7, 139.0, 138.6, 137.8, 135.2, 134.4, 132.3, 129.9, 129.8, 128.4, 127.8, 125.6, 122.2 (C arom), 101.7 (C ipso of 4-Tol) 93.0 (Cp), 75.9 (2-C of 4-Tol), 45.8 (*Me*CH), 32.0 (Me*C*H), 21.4 (4-Me). IR ν_{CO}: 1975, 1820.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bzpy)][Pd(Cl)] (20a). This complex was prepared by following the same procedure as for **20b**, starting from [Pd(bzpy)Cl]$_2$ (**13a**) and Cp(CO)$_2$Mo≡C-4-Tol (**3a**): total reaction time 24 h; orange powder (88%). Anal. Calcd for $C_{27}H_{22}ClMoNO_2Pd$ (M_r = 630.29) (+0.5CH_2Cl_2): C, 49.09; H, 3.33; N. 2.01. Found: C, 49.08; H, 3.16; N, 2.14. ^{1}H NMR ($CDCl_3$): ∂ 9.95 (d, 1 H arom, $^3J_{HH}$ = 5.8), 7.65–7.58 (m, 1 H arom), 7.41 (d, 1 H arom, $^3J_{HH}$ = 5.3), 7.34–7.24 (m, 5 H arom), 7.14–7.03 (m, 3 H arom), 6.68 (d, 1 H arom, $^3J_{HH}$ = 8.3), 4.60 (s, 5 H, Cp), 3.68, 3.57 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 13.2), 2.32 (s, 3 H, 4-Me). ^{13}C NMR ($CDCl_3$): ∂ 231.2, 226.5 (CO), 155.7 or 144.9 (μ-C), 155.3, 138.6, 138.1, 133.6, 132.9, 131.4, 129.5, 129.3, 128.0, 127.5, 125.3, 122.0 (C arom), 104.0 (C ipso of 4-Tol), 94.3 (Cp), 83.7 (2-C or 4-Tol), 45.2 (CH_2), 21.5 (4-Me). IR ν_{CO}: 1983, 1847.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bzpy)][Pd(I)] (20b). To a stirred suspension of [Pd(bzpy)I]$_2$ (**13b**; 481 mg, 0.60 mmol) in dichloromethane (30 mL) was added Cp(CO)$_2$Mo≡C-4-Tol (**3a**; 418 mg, 1.31 mmol). After 30 min, the solution was concentrated *in vacuo* to saturation and an excess of hexane (50 mL) was added. The precipitate was filtered off, washed with hexane (10 mL), and dried *in vacuo*. Complex **20b** was obtained as an orange powder (819 mg, 95%). Anal. Calcd for $C_{27}H_{22}IMoNO_2Pd$ (M_r = 721.74) (+0.25CH_2Cl_2): C, 44.05; H, 3.06; N, 1.89. Found: C, 44.31; H, 3.14; N, 1.78. ^{1}H NMR ($CDCl_3$): ∂ 10.14 (d, 1 H arom, $^3J_{HH}$ = 5.2), 7.63–7.53 (m, 2 H arom), 7.34–7.22 (m, 5 H arom), 7.13–7.01 (m, 3 H arom), 6.66 (d, 1 H arom, $^3J_{HH}$ = 8.9), 4.61 (s, 5 H, Cp), 3.70, 3.59 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 13.1), 2.32 (s, 3 H, 4-Me). ^{13}C NMR ($CDCl_3$): ∂ 230.8, 227.2 (CO), 160.1, 156.3 or 155.3 (μ-C), 144.8, 138.6, 133.8, 132.9, 131.2, 129.4, 128.8, 128.0, 127.6, 125.3, 122.0 (C arom), 103.3 (C ipso of 4-Tol), 94.3 (Cp), 83.7 (2-C of 4-Tol), 45.5 (CH_2), 21.5 (4-Me). IR ν_{CO}: 1988, 1845.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(bzpy)][Pd(Cl)] (20c). This complex was prepared by following the same procedure as for **20b**, but employing 3 equiv of Cp(CO)$_2$W≡C-4-Tol (**3b**) for 1 equiv of [Pd(bzpy)Cl]$_2$ (**13a**): total reaction time 16 h; orange powder (90%). Anal. Calcd for $C_{27}H_{22}ClNO_2PdW$ (M_r = 718.20) (+0.5CH_2Cl_2): C, 43.42; H, 3.23; N, 1.84. Found: C, 43.71; H, 3.08; N, 1.88. ^{1}H NMR ($CDCl_3$): ∂ 9.90 (d, 1 H arom, $^3J_{HH}$ = 4.6), 7.65–7.57 (m, 1 H arom), 7.51 (d, 1 H arom, $^3J_{HH}$ = 6.2), 7.34 (d, 1 H arom, $^3J_{HH}$ = 7.7), 7.26–7.24 (m, 2 H arom), 7.15–7.05 (m, 4 H arom), 6.95, 6.69 (AB pattern, 2 H, $^3J_{HH}$ = 8.8, 4-Tol), 4.68 (s, 5 H, Cp), 3.70, 3.56 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 13.1), 2.32 (s, 3 H, 4-Me). ^{13}C NMR ($CDCl_3$): ∂ 219.1, 212.8 (CO), 156.1 or 145.3 (μ-C), 155.1, 138.5, 137.1, 134.7, 134.0, 132.0, 129.7, 129.4, 128.2, 127.5, 125.1, 121.9 (C arom), 101.3 (C ipso of 4-Tol), 92.5 (Cp), 75.4 (2-C of 4-Tol), 45.5 (CH_2), 21.3 (4-Me). IR ν_{CO}: 1974, 1847.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(bzpy)][Pd(I)] (20d). This complex was prepared by following the same procedure as for **20b**, starting from [Pd(bzpy)I]$_2$ (**13b**) and Cp(CO)$_2$W≡C-4-Tol (**3b**): total reaction time 2.5 h; orange powder (80%). Anal. Calcd for $C_{27}H_{22}INO_2PdW$ (M_r = 809.65) (+0.25CH_2Cl_2): C, 39.39; H, 2.74; N, 1.69. Found: C, 39.26; H, 2.76; N, 1.67. ^{1}H NMR ($CDCl_3$): ∂ 10.11 (d, 1 H arom, $^3J_{HH}$ = 5.6), 7.65–7.57 (m, 2 H arom), 7.34 (d, 1 H arom, $^3J_{HH}$ = 7.8), 7.24–7.00 (m, 3 H arom), 7.18–7.00 (m, 3 H arom), 6.96 (d, 1 H arom, $^3J_{HH}$ = 7.6), 6.65 (d, 1 H arom, $^3J_{HH}$ = 8.9), 4.69 (s, 5 H, Cp), 3.72, 3.58 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 12.9), 2.33 (s, 3 H, 4-Me). ^{13}C NMR (400 MHz, CD_2Cl_2): ∂ 239.1, 231.6 (CO), 169.0 or 143.1 (μ-C), 160.8, 146.2, 140.3, 139.9, 133.3, 131.6, 131.2, 131.1, 129.0, 128.0, 127.1, 122.2 (C arom), 102.7 (C ipso of 4-Tol), 93.7 (Cp), 90.5 (2-C of 4-Tol), 48.9 (CH_2), 21.5 (4-Me). IR ν_{CO}: 1977, 1845.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bzpy)][Pd(OAc)] (20e). To a stirred suspension of [Pd(bzpy)OAc]$_2$ (**13c**; 373 mg, 0.56 mmol) in dichloromethane (40 mL) was added Cp(CO)$_2$Mo≡C-4-Tol (**3a**; 383 mg, 1.20 mmol). After 2.5 h, the solution was concentrated *in vacuo* to saturation, and an excess of hexane (40 mL) was added. The precipitate was filtered off, washed with hexane (20 mL), and dried *in vacuo*. Complex **20e** was obtained as an orange powder (510 mg, 70%). Anal. Calcd for $C_{29}H_{25}MoNO_4Pd$ (M_r = 653.89) (+CH_2Cl_2): C, 48.77; H, 3.69; N, 1.90. Found: C, 48.61; H, 3.37; N, 1.93. ^{1}H NMR ($CDCl_3$): ∂ 8.89 (d, 1 H arom, $^3J_{HH}$ = 5.4), 7.89 (d, 1 H arom, $^3J_{HH}$ = 5.3), 7.63–7.56 (m, 1 H arom), 7.36–7.22 (m, 5 H arom), 7.10–6.96 (m, 3 H arom), 6.63 (d, 1 H arom, $^3J_{HH}$ = 8.7), 4.59 (s, 5 H, Cp), 3.68, 3.54 (AB pattern, 2 H, CH_2, $^2J_{HH}$ = 12.9), 2.29 (s, 3 H, 4-Me), 2.05 (s, 3 H, O_2CMe). ^{13}C NMR ($CDCl_3$): ∂ 232.7, 227.5 (CO), 177.8 ($CH_3C(O)O$), 156.0 or 145.5 (μ-C), 152.5, 138.4, 137.3, 134.1, 132.3, 129.3, 128.9, 128.0, 127.8, 127.1, 125.2, 122.0 (C arom), 104.3 (C ipso of 4-Tol), 93.8

Table 3. X-ray Experimental Data

formula	$C_{28}H_{23}O_2SClPdW$
mol	749.3
color	red
cryst syst	monoclinic
a (Å)	11.324(3)
b (Å)	17.376(5)
c (Å)	12.589(3)
β (deg)	94.19(2)
V (Å^3)	2470.4
Z	4
D_{calc} (g cm^{-3})	2.014
wavelength (Å)	0.7107
μ (cm^{-1})	56.876
space group	$P2_1/n$
diffractometer	Enraf-Nonius CAD4-F
cryst dimens (mm)	0.18 × 0.20 × 0.40
temp (°C)	20
radiation	Mo Kα graphite monochromated
mode	$\theta/2\theta$
scan speed	variable
scan width (deg)	1.20 + 0.34 tan *θ*
octants	$\pm h,+k,+l$
θ(min/max) (deg)	2/24
no. of data collected	4706
no. of data with $I > 3\sigma(I)$	3346
abs min/max	0.79/1.00
R(*F*)	0.019
$R_w(F)$	0.027
p	0.04
GOF	1.031

Table 4. Positional and Thermal Parameters and Their Esd's

atom	*x*	*y*	*z*	*B* (Å^2)^a
W	0.80767(1)	0.90407(1)	0.84363(1)	1.949(3)
Pd	0.99657(3)	0.90259(2)	0.72494(2)	2.111(6)
Cl	1.1451(1)	1.00132(7)	0.7308(1)	3.63(2)
S	1.06258(9)	0.84482(6)	0.56596(8)	2.44(2)
C_1	0.8283(4)	1.0147(3)	0.8071(4)	3.19(9)
O_1	0.8348(4)	1.0787(2)	0.7905(3)	5.40(9)
C_2	0.9773(4)	0.9116(2)	0.8999(3)	2.68(8)
O_2	1.0592(3)	0.9150(2)	0.9597(3)	4.07(8)
C_3	0.8727(3)	0.8196(2)	0.7366(3)	2.01(7)
C_4	0.7114(5)	0.8179(3)	0.9488(5)	5.0(1)
C_5	0.7852(5)	0.8628(4)	1.0146(4)	5.4(1)
C_6	0.7466(5)	0.9392(3)	1.0057(4)	4.3(1)
C_7	0.6473(4)	0.9393(3)	0.9339(4)	3.9(1)
C_8	0.6276(4)	0.8639(3)	0.8997(4)	4.1(1)
C_9	0.7569(3)	0.8321(2)	0.6844(3)	2.12(7)
C_{10}	0.7230(4)	0.9087(2)	0.6528(3)	2.53(8)
C_{11}	0.6007(4)	0.9251(3)	0.6283(4)	3.29(9)
C_{12}	0.5164(4)	0.8700(3)	0.6268(4)	3.5(1)
C_{13}	0.5530(4)	0.7924(3)	0.6482(4)	3.6(1)
C_{14}	0.6658(4)	0.7736(2)	0.6780(4)	2.80(8)
C_{15}	0.3883(5)	0.8864(4)	0.5977(5)	5.4(1)
C_{16}	0.9317(3)	0.7434(2)	0.7438(3)	2.31(8)
C_{17}	0.9792(4)	0.7155(3)	0.8413(4)	3.25(9)
C_{18}	1.0427(5)	0.6474(3)	0.8494(4)	4.0(1)
C_{19}	1.0582(5)	0.6049(3)	0.7589(4)	4.1(1)
C_{20}	1.0107(4)	0.6315(2)	0.6617(4)	3.23(9)
C_{21}	0.9475(4)	0.7006(2)	0.6514(3)	2.44(8)
C_{22}	0.9037(4)	0.7257(2)	0.5430(3)	2.50(8)
C_{23}	0.8220(4)	0.6809(3)	0.4848(4)	3.31(9)
C_{24}	0.7804(5)	0.7003(3)	0.3817(4)	4.3(1)
C_{25}	0.8229(4)	0.7655(3)	0.3351(4)	4.1(1)
C_{26}	0.9055(4)	0.8114(3)	0.3902(4)	3.3(1)
C_{27}	0.9474(3)	0.7917(2)	0.4942(3)	2.31(7)
C_{28}	1.1005(4)	0.9177(3)	0.4742(4)	3.5(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\,\beta\,(1,2) + ac(\cos\beta)\,\beta\,(1,3) + bc\,(\cos\alpha)\,\beta\,(2,3)]$.

(Cp), 84.3 (2-C of 4-Tol), 45.4 (CH_2), 24.6 ($\mathit{C}H_3C(O)O$), 21.4 (4-Me). IR ν_{CO}: 1979, 1840.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bpdma)][Pd(Cl)] (21a). To a stirred suspension of [Pd(bpdma)Cl]$_2$ (**14**; 229 mg, 0.34 mmol) in dichloromethane (25 mL) was added $Cp(CO)_2Mo{\equiv}C$-4-Tol (**3a**; 230 mg, 0.72 mmol), and the color changed immediately to deep red-brown. After 15 min, the deeply colored mixture was filtered over a Celite pad, and the filtrate was concentrated *in vacuo* to 8 mL. An excess of hexane (40 mL) was added, and the solution was concentrated *in vacuo* until a precipitate formed. Hexane (20 mL) was added; the precipitate was filtered off and washed with hexane (20 mL). Drying *in vacuo* gave **21a** as a red powder (132 mg, 29%). Anal. Calcd for $C_{29}H_{26}ClMoNO_2Pd$ (M_r = 658.35) (+CH_2Cl_2): C, 48.46; H, 3.76; N, 1.88. Found: C, 48.14; H, 3.84; N, 1,74. ^{1}H NMR ($CDCl_3$): δ 7.58–7.27 (m, 4 H arom), 6.98–6.87 (m, 6 H arom), 6.77, 6.49 (AB pattern, 2 H, $^3J_{HH}$ = 8.8), 4.42 (s, 5 H, Cp), 2.99, 2.63 (2 s(b), 6 H, NMe_2), 2.19 (s, 3 H, 4-Me). ^{13}C NMR ($CDCl_3$): δ 236.2, 227.8 (CO), 166.1 or 153.5 (μ-C), 140.7, 138.2, 135.9, 135.4, 133.0, 131.5, 129.9, 129.4, 129.2, 129.0, 128.0, 124.7, 117.0 (C arom), 102.9 (C ipso of 4-Tol), 94.1 (Cp), 87.0 (2-C of 4-Tol), 48.5 (br, NMe_2), 21.4 (4-Me). IR ν_{CO}: 1973, 1822.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(bpdma)][Pd(Cl)] (21b). This complex was prepared by following the same procedure as for **21a**, starting from [Pd(bpdma)-Cl]$_2$ (**14**) and $Cp(CO)_2W{\equiv}C$-4-Tol (**3b**): total reaction time 20 min, red powder (29%). Anal. Calcd for $C_{29}H_{26}ClNO_2PdW$ (M_r = 746.26) (+CH_2Cl_2): C, 43.33; H, 3.40; N, 1.69. Found: C, 43.46; H, 3.36; N, 1.69. ^{1}H NMR ($CDCl_3$): δ 7.57–7.41 (m, 3 H arom), 7.35 (d, 1 H arom, $^3J_{HH}$ = 8.8), 7.07 (d, 1 H arom, $^3J_{HH}$ = 6.4), 6.93–6.83 (m, 5 H arom), 6.70 (d, 1 H arom, $^3J_{HH}$ = 8.7), 6.49 (d, 1 H arom, $^3J_{HH}$ = 8.4), 4.51 (s, 5 H, Cp), 2.96 (s(b), 3 H, NMe), 2.63 (s(b), 3 H, NMe), 2.20 (s, 3 H, 4-Me). ^{13}C NMR ($CDCl_3$): δ 224.8, 214.8 (CO), 153.4 or 152.4 (μ-C), 141.5, 137.3, 137.1, 135.5, 133.1, 132.9, 132.4, 130.3, 129.6, 129.4, 129.0, 128.5, 127.9, 124.4, 116.8 (C arom), 100.6 (C ipso of 4-Tol), 92.4 (Cp), 79.2 (2-C of 4-Tol), 48.8 (br, NMe_2), 21.2 (4-Me). IR ν_{CO}: 1966, 1820.

[Cp(CO)(μ-CO)Mo][μ-C(4-Tol)(bpms)][Pd(Cl)] (22a). To a stirred solution of [Pd(bpms)Cl]$_2$ (**15**; 212 mg, 0.31 mmol) in dichloromethane (20 mL) was added $Cp(CO)_2Mo{\equiv}C$-4-Tol (**3a**; 212 mg, 0.66 mmol). After 15 min, the solution was concentrated *in vacuo* to saturation and an excess of hexane (30 mL) was added. The precipitate was filtered off, washed with hexane (5 mL), and dried *in vacuo*. Complex **22a** was obtained as a light orange powder (309 mg, 75%). Anal. Calcd for $C_{28}H_{23}ClMoO_2PdS$ (M_r = 661.37): C, 50.85; H, 3.51; S, 4.85. Found: C, 51.0; H, 3.7; S, 4.9. ^{1}H NMR ($CDCl_3$): δ 7.52 (m, 3 H arom), 7.25 (m, 1 H arom), 7.13–6.92 (m, 6 H arom), 6.79, 6.61 (AB pattern, 2 H arom, $^3J_{HH}$ = 8.9), 4.47 (s, 5 H, Cp), 2.43 (s, 3 H, Me), 2.20 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 234.4, 228.8 (CO), 161.7 (μ-C), 144.5, 143.9, 142.9, 138.7, 134.1, 133.8, 133.7, 132.2, 131.8, 131.0, 130.3, 130.0, 129.5, 129.3, 129.2, 128.2, 127.3, 126.6 (C arom), 103.0 (C ipso of 4-Tol), 94.1 (Cp), 89.3 (2-C of 4-Tol), 21.3, 18.9 (Me). IR ν_{CO}: 1975, 1831.

[Cp(CO)(μ-CO)W][μ-C(4-Tol)(bpms)][Pd(Cl)] (22b). This complex was prepared by following the same procedure as for **22a**, starting from [Pd(bpms)Cl]$_2$ (**15**) and $Cp(CO)_2W{\equiv}C$-4-Tol (**3b**): total reaction time 35 min; light orange powder (86%). Anal. Calcd for $C_{28}H_{23}ClO_2PdSW$ (M_r = 749.28): C, 44.88; H, 3.09. Found: C, 44.82; H, 3.19. ^{1}H NMR ($CDCl_3$): δ 7.55–7.47 (m, 3 H arom), 7.26–7.23 (m, 1 H arom), 7.13 (d, 1 H arom, $^3J_{HH}$ = 6.4), 7.06–6.95 (m, 4 H arom), 6.86 (d, 1 H arom,

$^3J_{HH}$ = 6.4), 6.73 (d, 1 H arom, $^3J_{HH}$ = 9.6), 6.60 (d, 1 H arom, $^3J_{HH}$ = 8.2), 4.55 (s, 5 H, Cp), 2.46 (s, 3 H, Me), 2.20 (s, 3 H, Me). ^{13}C NMR (400 MHz, $CDCl_3$): ∂ 221.1, 214.9 (CO), 147.4 or 144.8 (μ-C), 142.4, 137.5, 135.4, 134.1 (C_{quat} arom), 133.6, 132.1, 131.5, 130.4, 130.0, 129.4, 129.3, 129.2, 127.6, 127.4, 125.3 (C—H arom), 100.6 (C ipso of 4-Tol), 92.6 (Cp), 80.2 (2-C of 4-Tol), 21.2 (4-Me), 18.2 (SMe). IR ν_{CO}: 1967, 1832.

Structure Determination and Refinement of Compound 22b. Suitable single crystals of **22b** were obtained by slow evaporation of a CH_2Cl_2/*n*-hexane solution at −20 °C. One single crystal was cut out from a cluster of crystals and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using an Enraf-Nonius CAD4-F automatic diffractometer showed that crystals of **22b** belong to the monoclinic system. Quantitative data were obtained at room temperature. All experimental parameters used are given in Table 3. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package was used.[33] Three standard reflections measured every 1 h during the entire data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz and polarization factors. Absorption corrections computed from the Φ scans of four reflections were applied. The structure was solved using the heavy atoms. A difference-Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C−H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1.3B_{eqv}(C)$ Å^2 but not refined. Full least-squares refinements were used: $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 34.

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Supplementary Material Available: Tables of bond distances and angles, positional parameters of H atoms, and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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[33] Frenz, B. A. The Enraf-Nonius CAD4-SPD. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64−71.

[34] (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2b. (b) Table 2.3.1.