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Multinuclear NMR Studies and Reaction with *tert*-Butyl Isocyanide of Dinuclear Tungsten– or Molybdenum–Palladium μ-Alkylidene Complexes. X-ray Structure of [PdI{μ-C(*p*-tolyl)dmba}{μ-CO}Mo(Cp)(CN-*t*-Bu)₂]

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The ^{1}H,^{13}C, and ^{183}W NMR characteristics for a series of dinuclear complexes containing a W–(μ-CR^{1}R^2)–Pd moiety are reported. These compounds, derived from the reaction of the carbyne complex (Cp)(CO)$_2$M(≡CR), M = Mo, W, R = cyclopentenyl or *p*-tolyl, with a dinuclear cyclopalladated complex are shown to possess an η^2-bond from the cyclopentenyl or *p*-tolyl fragment to the metal, thus attaining an 18-electron configuration at M. The bridging carbon has its ^{13}C absorption at $\delta = 142.4-155.1$. Reaction of a Mo derivative with 2 equiv of *t*-BuNC displaces the η^2-bond and affords a new complex, [PdI{μ-C(*p*-tolyl)-dmba}{μ-CO}Mo(Cp)(*t*-BuNC)$_2$], whose structure in the solid state was determined by X-ray diffraction. The solution NMR data for this complex clearly show that the η^2-bond is no longer present.

Introduction

The organometallic chemistry of olefin complexes remains a field of active research.[1] One rather special subclass concerns the chemistry of η^2-aromatic complexes, which, although rare, are increasingly recognized.[2,3]
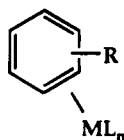
fragment showing an η^2-aromatic complex

Recently,[4] some of us have been involved in the preparation and characterization of the unusual dinuclear complexes that can be prepared from the reaction of several different halogen-bridged cyclometalated com-

plexes of Pd(II) with the tungsten carbyne complex W(Cp)(CO)$_2$(≡CR), where R is the cyclopentenyl fragment C$_5$H$_7$ or the *p*-tolyl fragment C$_7$H$_7$. Examples of these products are **1–4**, with **4** having been characterized by X-ray crystallography. Analogous Mo complexes exist as well.

The immediate nature of the formerly carbyne carbon in **1–4** is not obvious. One can consider this bridging carbon ligand as formally a dianion, i.e., an [R^{1}R^{2}C]$^{2-}$-type donor, in which case the carbon might approach sp^3 hybridization. This formalism would result in the assignment of Pd(II) and W(II) as the appropriate oxidation states for the metals. The observation of a quaternary ^{13}C signal at ~100 ppm seemed consistent with this approach.[5]

We report here ^{1}H,^{13}C, ^{183}W, and NOESY NMR results which suggest that the above structures should be modified to include coordination of the double bond of the C$_5$H$_7$ or one of the C$_7$H$_7$ double bonds, thereby producing a complex whose structure contains an η^2-olefin moiety.

Results and Discussion

Chart 1 shows the complexes studied, and Table 1 shows selected ^{13}C and ^{183}W NMR data. We give full ^{1}H and ^{13}C data for **1, 2, 10,** and **13a** in Tables 2 and 3.

⊛ Abstract published in *Advance ACS Abstracts,* March 1, 1995.
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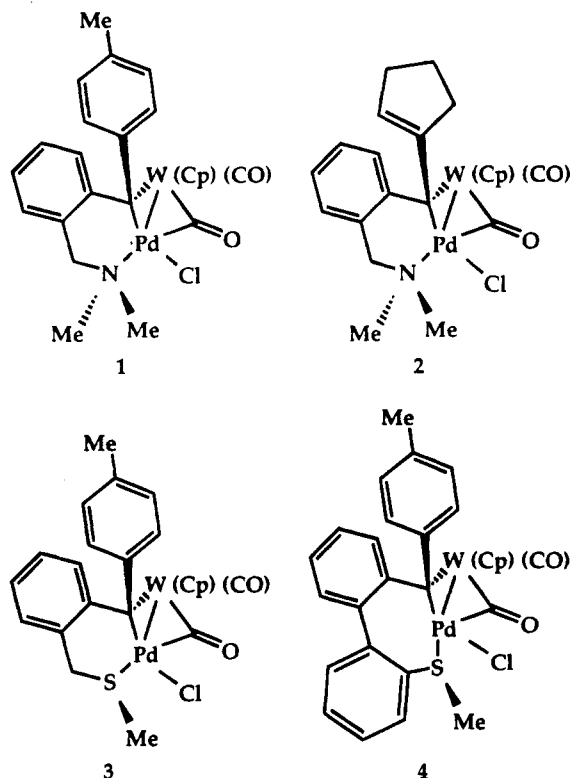(4) Engel, P. F.; Pfeffer, M.; Fischer, J. *Organometallics* **1994,** *13,* 4751.

(5) (a) Herrmann, W. A. *Adv. Organometallic Chem.* **1982,** *20,* 159. (b) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980,** 1593.

1   2

3   4

Modified View of the Bonding in 1–10.

We became aware of a possible η^2-interaction involving the double bond of the cyclopentenyl group in **2** via a 2-D ^{1}H NOESY spectrum, a section of which is shown in Figure 1. An analysis of the cross-peaks reveals face-selective NOEs which arise from the two distinct faces of this C_5H_7 ligand when coordinated. A similar selectivity was also found to be present for the *p*-tolyl complexes. Indeed, inspection of the ^{1}H and ^{13}C spectra for these *p*-tolyl compounds reveals four ^{1}H and six ^{13}C *p*-tolyl signals, so that here, as well, there is restricted rotation about the μ-C–C(7) bond. In addition, the 2-D ^{1}H NOESY spectrum proved valuable in the assignment of the aromatic protons and, subsequently, via a ^{13}C, ^{1}H correlation, the pertinent ^{13}C signals.
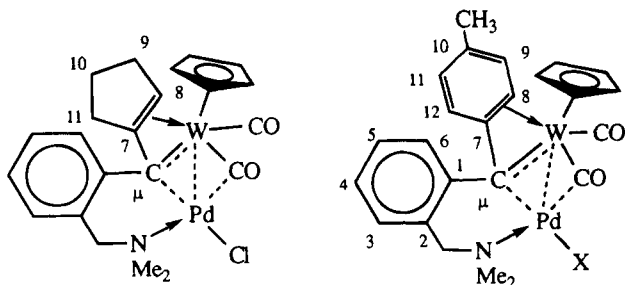

A routine ^{13}C, ^{1}H correlation for **2**, shown in Figure 2, revealed that the ^{13}C resonance for the protonated olefinic carbon appeared at $\delta = 60.8$, a much lower frequency than is expected if the double bond were not coordinated, but normal[6] for a W(II) olefin complex. The assignment of the quaternary μ-C and C(7) resonances followed from a long-range ^{13}C, ^{1}H correlation, a section of which is also reproduced in Figure 2. From the observed two- (and the more reliable) three-bond

J(^{13}C,^{1}H)-values,[7] we see that the μ-C resonance appears at 147.6 ppm (the total range for our complexes is 142.4–155.1 ppm) whereas C(7) is at 109.7 ppm. Consequently, the signal at ~100 ppm, mentioned above, is C(7) and *not* the bridging carbon. Similar ^{13}C results were found for the *p*-tolyl complexes **1** and **3–9** (see Table 1). We note that the μ-^{13}C signal for **6** ($\delta = 155.1$), which has a terminal PMe$_2$Ph on Pd(II) in pseudo trans position to the μ-C atom, appears as a doublet, ${}^2J({}^{31}P,{}^{13}C)_{trans} = 56.4$ Hz. Adams et al.[8] reported ^{13}C shifts of 98.5, 80.2 and 52.1 ppm for the coordinated allyl carbons in the η^3-benzyl complex CpW{η^3-C$_6$H$_5$CH(OEt)}(CO)$_2$, with the 98.5 ppm value for the ipso carbon. Further, Su and Wojcicki[9] give ^{13}C shifts of 61.1 and 90.7 ppm for the two aromatic carbons of the η^3-benzyl derivative CpW(CO)$_2$(η^3-CH(CH$_3$)Ph). On the basis of our μ-C ^{13}C data, we do not believe that we have an η^3-complex; however, we consider our aromatic ^{13}C chemical shift data to be in good agreement with what one would expect for two coordinated aryl carbons in a tungsten(II) complex.

Interestingly, the olefinic CH proton, H(8), in **2**, $\delta = 5.26$, is only moderately shifted away from its position, e.g., in cyclopentene, $\delta = 5.60$, and qualitatively, the same modest change is observed for the aromatic ortho proton of the coordinated double bond, $\delta = 6.72$ in **1**.

Our ^{13}C assignments require that, relative to the sketches **1–4**, the bonding for both the double bond and the bridging carbon atom be reconsidered. We suggest η^2-interactions of the following type:

A   B
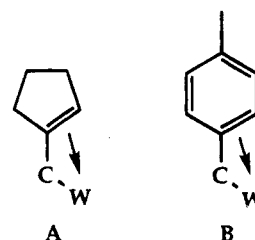
Coordination of the appropriate double bond leads to 18-electron configurations at the tungsten atoms and, of course, restricted rotation about the μ-C–C(7) bond. It is pertinent that, in their discussion of the reactive species Cp(CO)$_2$W(CH=Tol)$^+$, which arises from the protonation of the analogous carbyne complex, Garrett et al.[10] mentioned an η^3-carbene as a structural possibility but offered no proof of its existence.

The exact nature of the bridging carbon atom in **1–10** remains open. In the absence of evidence to the contrary, we consider this atom as having some bridging carbene character, in analogy with the literature.[5] For the dinuclear bridging carbene complex
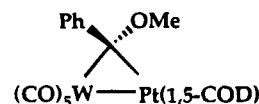
Ashworth et al.[5b] found the bridging carbene ^{13}C signal

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Chart 1
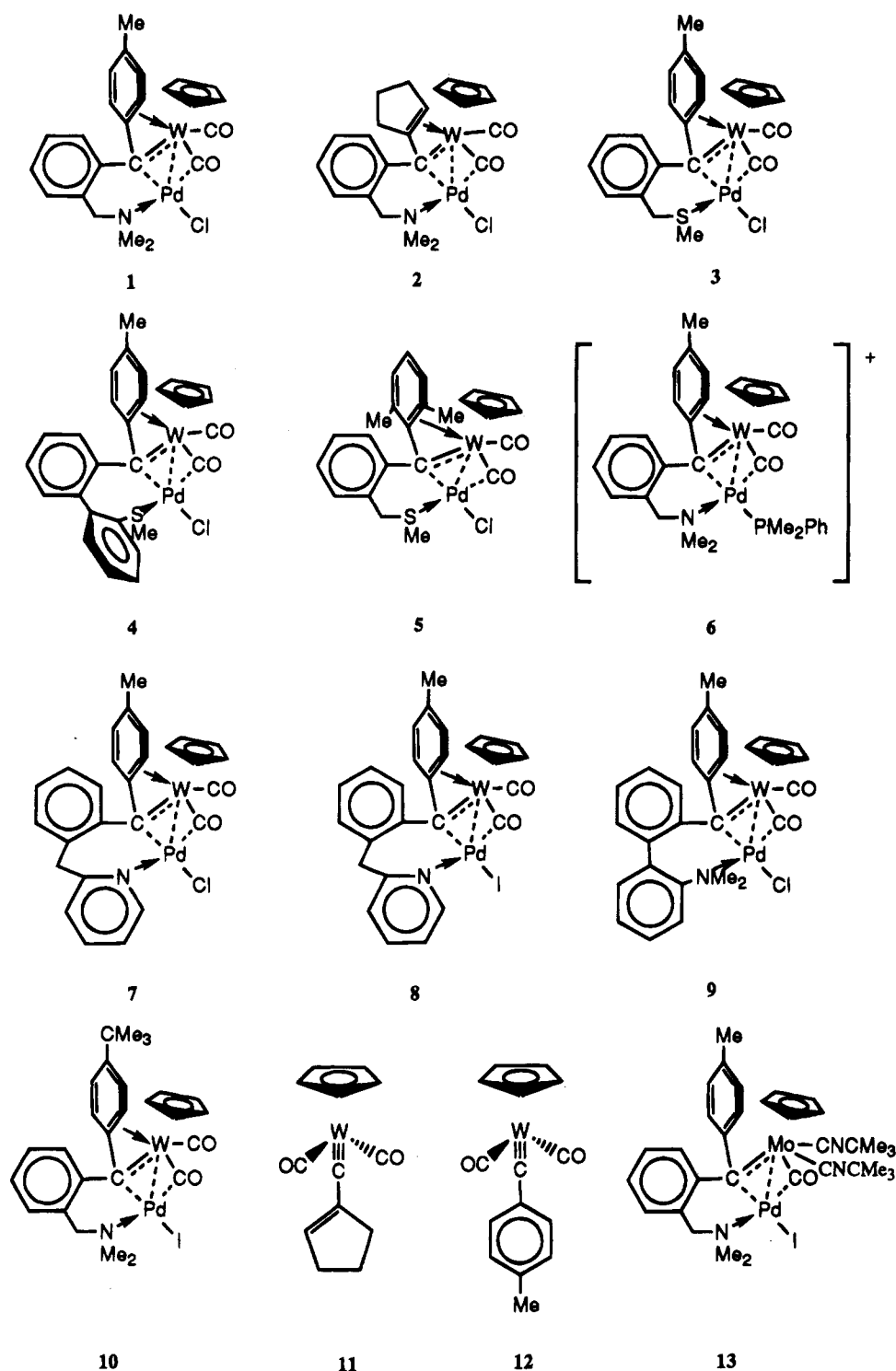
at 197 ppm, too high a frequency for a simple sp³ carbon. Our µ-¹³C chemical shifts are not consistent with the ¹³C characteristics for an η³-benzyl-type ligand in that they come at too high a frequency.[11,12] However, these same δ values are too low in frequency for normal tungsten−carbene complexes.[13]

Further, in the X-ray structure[4] for **4**, the W−(µ-C) separation is 2.158(4) Å and the Pd−(µ-C) separation is 2.024(4) Å. The former is not suggestive of W=C character, but is somewhat short for a W−C single bond,[10] and the latter is quite reasonable for a Pd−C σ-bond.

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Table 1. ¹⁸³W and Relevant ¹³C NMR Data

	δ^{183}W (ppm)	$\delta^{13}C^a$ (ppm)		
		μ-C	C(7)	C(8)
1	−1877	142.4	101.8	76.5
2	−2244	147.6	109.7	60.8
3	−1880	144.3	103.2	77.7
4	−1836	144.8^b	100.6	80.1
5	−1925	146.4^b	100.4	83.7
6	−1893	155.1	100.2	78.9
7	−2033	145.2	101.3	75.3
8	−1975	na^d	102.7	90.5^{b,c}
9	−1825	na	100	78^b
10	−1852	145.4	101.3	74.6
11	−1921			
12	−1950			
13		148.7	158.2	122.1

^{a} CDCl₃. ^{b} Tentative assignment from Ph.D. Thesis of P.F.E. ^{c} CD₂Cl₂. ^{d} na, not assigned.

Table 2. ¹³C NMR Data^a (ppm) for 1, 2, 10, and 13a

	1	2	10	13a
C(1)	146.2	145.4	145.8	159.4
C(2)	136.6	135.1	136.8	136.1
C(3)	130.8	130.3	130.8	130.2
C(4)	126.5	126.4	126.6	124.1
C(5)	129.6	129.6	129.7	127.4
C(6)	128.3	126.3	128.4	133.1
C(7)	101.8	109.7	101.3	158.2
C(8)	76.5	60.8	74.6	122.1
C(9)	132.0	31.8	127.8	127.4
C(10)	137.5	22.1	150.7	132.1
C(11)	133.9	33.2	130.9	128.2
C(12)	127.2		127.1	129.1
CH₃	21.4			20.8
C(CH₃)			30.8	
CMe₃			35.1	
μ-C	142.4	147.6	145.4	148.7
CH₂	68.3	68.6	68.1	66.1
NMe₂	47.3	47.3	49.5	49.5
	51.1	51.3	52.5	52.4
Cp	91.6	90.7	91.8	91.9
CO	215.6	212.2	215.3	249.4
	222.0	221.4	221.3	
CNCMe₃				162.8
				160.4
CNCMe₃				57.2
				58.4
CNCMe₃				30.2
				30.9

^{a} CDCl₃.

¹⁸³W NMR. The ¹⁸³W literature is relatively sparse;[14-27] however, we recently suggested[14,15] that inverse detection methodology readily allows access to

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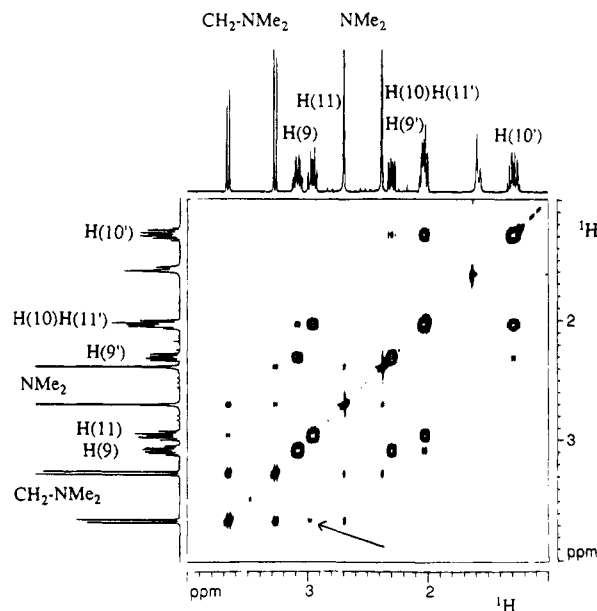(27) Sekino, M.; Sato, M.; Nagasawa, A.; Kikuchi, K. *Organometallics* **1994**, *13*, 1451.

Figure 1. Section of the 2-D ¹H NOESY spectrum for **2**, showing the six nonequivalent protons on C(9)−C(11) of the cyclopentenyl fragment. The primed protons face tungsten. Note the weak cross-peak (arrow) from the nonprimed proton H(11) to one of the NCH₂ protons, thus assigning the two faces.

Table 3. ¹H NMR Data^a (ppm) for 1, 2, 10, and 13a

	1	2	10	13a
H(3)	7.29	7.28	7.31	6.98
H(4)	7.29	7.22	7.30	7.05
H(5)	7.43	7.32	7.44	7.24
H(6)	7.05	6.86	7.07	7.19
H(8)	7.46	5.26	7.46	6.02
H(9)	7.14	3.08	7.27	6.61
H(9′)		2.30		
H(10)		2.02		
H(10′)		1.28		
H(11)	6.95	2.95	7.21	7.02
H(11′)		2.03		
H(12)	6.73		6.74	8.22
CH₃	2.32			2.15
CMe₃			1.29	
CH₂	3.28	3.66	3.37	3.24
	3.11	3.27	3.15	2.65
NMe₂	2.52	2.69	2.59	2.97
	2.38	2.38	2.43	2.43
Cp	4.70	5.34	4.67	4.60
CNCMe₃				1.58
				1.16

^{a} CDCl₃.

the ¹⁸³W metal resonances for a variety of organometallic tungsten complexes and show such a spectrum for **2** in Figure 3. Specifically, we have been able to obtain chemical shift data for Cp, Tp′(= 3,5-dimethyltris-(pyrazolyl)borate), allyl, acetylene, and imido (≡NPh) tungsten complexes, among others.[14,15] Table 1 also shows ¹⁸³W chemical shifts for the binuclear complexes **1−10** as well as data for the model carbyne complexes **11** and **12**.

There are several interesting points concerned with these ¹⁸³W chemical shifts:

(1) All of the chemical shifts come at relatively low frequency, in the range −1825 to −2244 ppm relative to WF₆. The resonance positions for the coordinatively saturated W(0) complexes W(Cp)(CO)₃⁻,[14a] WH(NO)-(CO)₂(PEt₃)₂,[24] and W(CO)₆[18] are −2298, −1441, and −2340 ppm, respectively, i.e., in the same region.
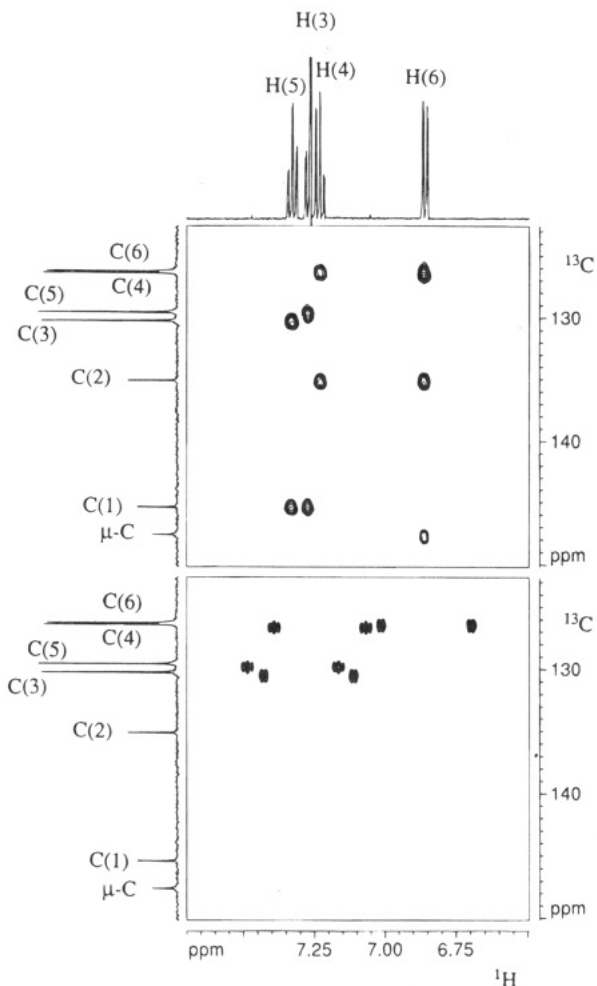
Figure 2. Section from (a) the *long-range* ¹³C–¹H inverse correlation (upper part) and (b) the *conventional* ¹³C–¹H inverse correlation (lower part) for **2**. Note the correlation of the bridging carbon ¹³C signal to H(6), in the upper spectrum, thereby helping to identify this resonance. The ipso carbon C(1) correlates to both H(3) and H(5).

Further, the coordinatively saturated compounds, W(Et)-(Cp)(CO)₃,[16] and W(η³-C₃H₅)₄[21] have their absorptions at δ = −2358 and −2069, also relatively close to those we find. The model carbyne complexes W(Cp)(≡CR)-(CO)₂, δ = −1921 and −1950, for R = C₅H₇ and *p*-tolyl, **11** and **12**, respectively, fall in the range found for **1−10**. The various observed differences between **1−12** are modest given that the total range of ¹⁸³W chemical shifts is ~11 000 ppm.[16−27] We consider our ¹⁸³W chemical shifts for **1−10** to be consistent with an 18-electron, coordinatively saturated, electronic structure, i.e., having an additional double bond donor and possessing a relatively large HOMO−LUMO gap, such that the $1/(E_i - E_j)$ term in the paramagnetic shielding expression is relatively large. Assuming[17] the ¹⁸³W resonance frequency ν to be

$$\nu = \propto (1 - \sigma_P)$$

$$\sigma_P = \propto - \sum (E_i - E_j)^{-1}$$

then a relatively large $(E_i - E_j)$ affords a low-frequency position. Coordinatively unsaturated complexes afford much higher frequency ¹⁸³W absorptions, e.g., for W₂(CF₃-CO₂)₄,[18b] δ = +5643, for W(NEt)Cl₄(Et₂O),[14] δ = +2382,
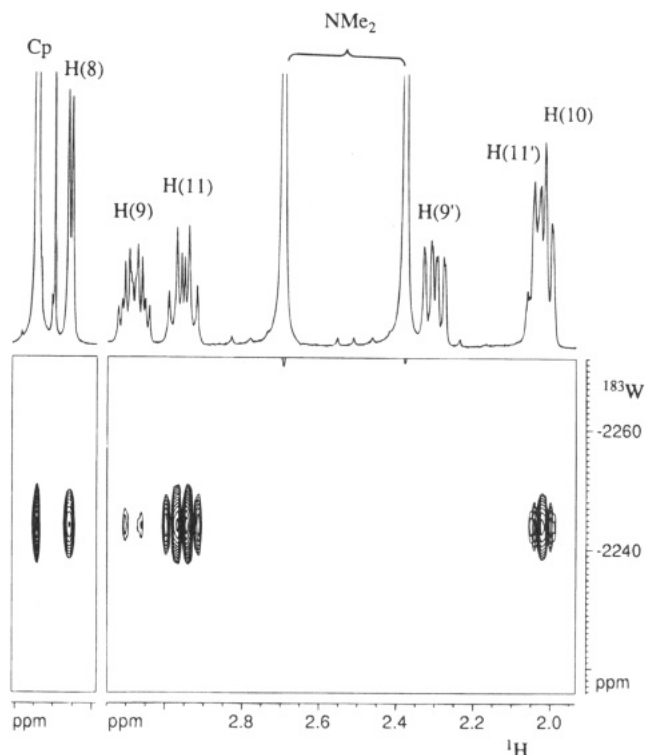

Figure 3. Proton−tungsten correlation for **2**, showing interactions of the ¹⁸³W with the Cp protons, H(8), H(11), and presumably H(10). All of these $^nJ(^{183}W,^1H)$ values are not visible in the 1-D spectrum.

**Table 4. Selected Bond Distances (Å) and Angles (deg) for 13a**

Bond Distances					
Pd(2)−I(1)	2.737 (2)	C(6)−C(17)	1.53 (2)	Mo(3)−C(6)	2.21 (1)
Pd(2)−C(4)	2.12 (2)	C(24)−N(25)	1.19 (2)	C(4)−O(5)	1.18(2)
Pd(2)−N(14)	2.20 (1)	Pd(2)−Mo(3)	2.692 (2)	C(6)−C(7)	1.51 (2)
Mo(3)−C(24)	2.06 (2)	Pd(2)−C(6)	2.02 (2)	C(30)−N(31)	1.11 (2)
Mo(3)−C(30)	2.14 (2)	Mo(3)−C(4)	1.98 (2)		

Bond Angles				
N(14)−Pd(2)−I(1)	118.94 (7)	N(14)−Pd(2)−C(4)	161.4 (6)
C(4)−Pd(2)−I(1)	90.1 (5)	C(6)−Pd(2)−I(1)	172.5 (4)
C(6)−Pd(2)−C(4)	83.6 (6)	C(6)−Mo(3)−C(4)	82.4 (6)
N(14)−Pd(2)−C(6)	93.5 (5)	C(24)−Mo(3)−C(6)	134.9 (6)
C(24)−Mo(3)−C(4)	80.1 (7)	C(30)−Mo (3)−C(4)	120.9 (7)
C(7)−C(6)−Mo(3)	120.8 (11)	C(30)−Mo (3)−C(24)	73.8 (7)
C(17)−C(6)−Mo(3)	119.2 (10)	O(5)−C(4)−Mo(3)	154.4 (11)
C(7)−C(6)−Pd(2)	114.3 (10)	C(17)−C(6)−Pd(2)	115.7 (10)
C(17)−C(6)−C(7)	106.1 (12)	N(25)−C(24)−Mo(3)	175.8 (15)
N(31)−C(30)−Mo(3)	172.5 (17)	C(32−N(31)−C(30)	171.2 (20)

and for W(Cp*)(=O)₂Me, δ = +464.9,[23] i.e., *thousands* of ppm to higher frequency.

(2) The small-to-modest changes in the ¹⁸³W chemical shifts for **1−10** support the formulation of these complexes as structurally similar with respect to the tungsten coordination sphere; i.e., the different halogens (or phosphine or cyclometalated N-donor, etc.) are indeed on palladium and not on tungsten.

(3) Complex **2** has the lowest metal resonance frequency, δ = −2244. We believe this arises due to a stronger interaction of the double bond in **2**, relative to the corresponding interaction in the *p*-tolyl complexes. We note in this connection that the ¹³C position for C(8) in **2** is also at the lowest frequency.

A Molybdenum Derivative. Since we postulate an interaction between a double bond of the *p*-tolyl group and the tungsten (and by analogy, an η²-bond to the molybdenum[4]), we considered a reaction to disrupt this
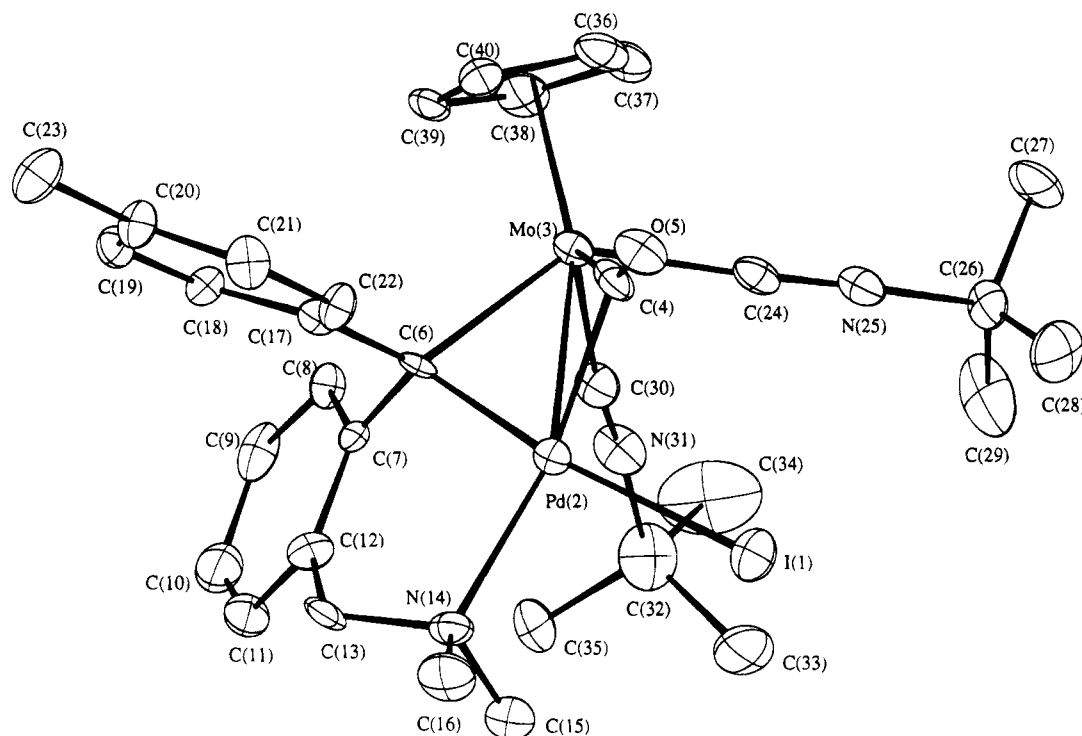
Figure 4. Cameron view for **13a**.

bond and decided on the isonitrile chemistry, shown:
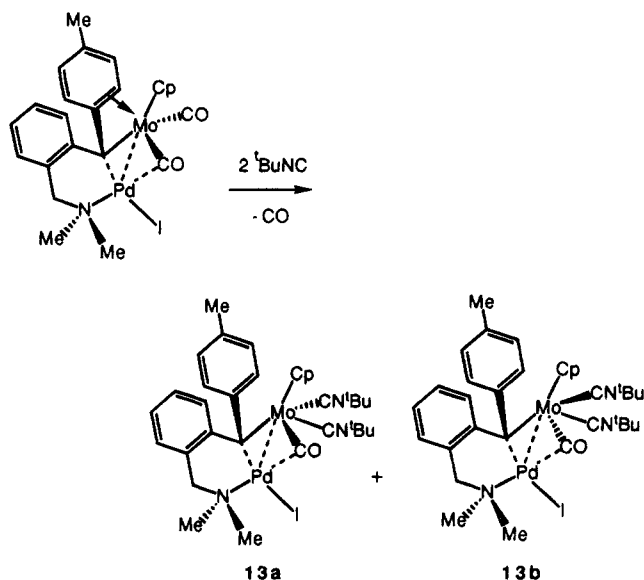
The addition of an excess of *t*-BuNC to the Mo—Pd analog, shown above, gave high yields of a mixture of two compounds after 2 days at room temperature (the analogous tungsten reaction was slow, leading to mixtures of mono- and di-*t*-BuNC adducts which were difficult to separate). **13a** and **13b** result from the addition of two isocyanide ligands and the displacement of one CO and were shown by ¹H NMR and infrared spectroscopy to be closely related, thus suggesting isomers. However, only **13a** could be obtained in a pure form by fractional crystallization as single crystals suitable for X-ray diffraction analysis. Complex **13b** was always contaminated by variable amounts of **13a**. Consequently, we have fully characterized **13a** and assign **13b** to a geometric isomer by comparison.

Table 5. Crystallographic Data for 13a

chemical formula	PdMoC₃₃H₄₂ON₃
fw	825.96
crystal system	monoclinic
space group	$P2_1/a$
Z	4
a, Å	18.091(4)
b, Å	10.928(7)
c, Å	16.970(3)
β, deg	95.61(1)
V, Å³	3339
$F(000)$	1640
ϱ(calcd), g cm⁻³	1.64
μ(Mo Kα), cm⁻¹	18.41
cryst size, mm	0.2 × 0.24 × 0.36
diffractometer	Philips PW1100
monochromator	graphite
radiation	Mo Kα (0.710 70)
temperature °C	20
scan type	$\omega/2\theta$
scan range θ, deg	1.10 + 0.34 tan θ
2θ range, deg	4−45
no. of reflctns collected	3693
no. of reflctn used (criteria)	2046 ($I > 3\sigma(I)$)
R	0.048
$R_w{}^a$	0.054
absorptn corr[b]	min 0.78, max 1.09
weighting scheme	unit weights
rms (shift/esd)	0.16
ls params	362
residual electron dens, e Å⁻³	0.69

[a] $R_w = [\sum_i w_i (F_o - F_c)^2 / \sum_i w_i F_0^2]^{1/2}$. [b] Difabs: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

The ORTEP plot of **13a** is given in Figure 4; selected bond lengths and bond angles are given in Table 4, crystallographic data in Table 5, and fractional parameters in Table 6.

If one neglects the Pd—Mo interaction (which at 2.692(2) Å, is ~0.1 Å shorter than in a number of Mo—

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Table 6. Fractional Parameters for PdIMoC₃₃H₄₂ON₃

atom	x/a	y/b	z/c	U(eq)
I(1)	0.80131(8)	0.0317(2)	0.70692(9)	0.0790
Pd(2)	0.94326(7)	0.0969(1)	0.76128(7)	0.0384
Mo(3)	1.03525(9)	0.1778(1)	0.65711(9)	0.0385
C(4)	0.983(1)	0.019(2)	0.6589(9)	0.0481
O(5)	0.9702(7)	−0.083(1)	0.6385(7)	0.0549
C(6)	1.0503(9)	0.148(1)	0.7863(8)	0.0284
C(7)	1.0614(8)	0.255(2)	0.8430(9)	0.0373
C(8)	1.1081(9)	0.356(1)	0.829(1)	0.0402
C(9)	1.121(1)	0.446(2)	0.887(1)	0.0579
C(10)	1.088(1)	0.443(2)	0.956(1)	0.0775
C(11)	1.043(1)	0.350(2)	0.968(1)	0.0577
C(12)	1.0301(9)	0.252(2)	0.914(1)	0.0409
C(13)	0.983(1)	0.147(2)	0.9385(9)	0.0432
N(14)	0.9167(8)	0.122(1)	0.8838(8)	0.0480
C(15)	0.864(1)	0.222(2)	0.888(1)	0.0797
C(16)	0.883(1)	0.007(2)	0.913(1)	0.0719
C(17)	1.1033(9)	0.047(1)	0.8200(9)	0.0377
C(18)	1.1707(8)	0.070(1)	0.8618(9)	0.0366
C(19)	1.2161(9)	−0.020(2)	0.8935(9)	0.0468
C(20)	1.201(1)	−0.143(1)	0.879(1)	0.0449
C(21)	1.132(1)	−0.165(2)	0.842(1)	0.0454
C(22)	1.0832(9)	−0.077(2)	0.812(1)	0.0428
C(23)	1.254(1)	−0.242(2)	0.913(1)	0.0678
C(24)	0.946(1)	0.213(2)	0.576(1)	0.0459
N(25)	0.8968(9)	0.239(1)	0.5266(8)	0.0578
C(26)	0.839(1)	0.292(2)	0.469(1)	0.0520
C(27)	0.872(1)	0.310(3)	0.392(1)	0.0802
C(28)	0.775(1)	0.201(2)	0.460(1)	0.0911
C(29)	0.815(2)	0.413(2)	0.502(1)	0.0947
C(30)	0.985(1)	0.342(2)	0.696(1)	0.0546
N(31)	0.958(1)	0.430(1)	0.7077(9)	0.0601
C(32)	0.913(1)	0.543(2)	0.734(1)	0.0931
C(33)	0.829(1)	0.539(3)	0.726(1)	0.0980
C(34)	0.924(2)	0.644(3)	0.672(2)	0.1298
C(35)	0.944(1)	0.616(4)	0.815(1)	0.1105
C(36)	1.097(1)	0.090(2)	0.563(1)	0.0593
C(37)	1.098(1)	0.217(2)	0.548(1)	0.0569
C(38)	1.138(1)	0.273(2)	0.611(1)	0.0627
C(39)	1.1636(9)	0.182(2)	0.6668(9)	0.0479
C(40)	1.138(1)	0.074(2)	0.635(1)	0.0502

Pd complexes[28,29]) then one can consider the palladium atom as being in a distorted square-planar environment defined by I(1), N(14), C(6), and C(4). The two isocyanide ligands are complexed to Mo, which is heptacoordinated (again neglecting the metal−metal bond). The geometry around this Mo atom is close to that of a four-legged piano stool. The interactions between the three atoms C(6), Mo(3), C(4) and the Pd(2) atom are similar to those found in a closely related dinuclear Pd−Mo complex, **14**, in which the Cp has been substituted by the tripod ligand, CpCo{P(OMe)₂O}₃⁻.[29] The Pd(2)−Mo(3) distance in **13a**, 2.2692(2) Å is shorter by 0.14 Å than that found for the CpCo{P(OMe)₂O}₃⁻ analog. However, the Mo(3)−C(6) bond in **13a**, 2.21(1) Å, is longer by ∼0.1 Å, than that found in **14**, 2.118(7) Å, with the former value being close to that of a normal Mo−C single bond, 2.24−2.41 Å.[30] The two isocyanides have a cis geometry (the C(24)−Mo−C(30) angle is 73.8(7)°), and the semibridging carbonyl group, C(4)O(5) is in a syn position with respect to the p-tolyl unit.

Given the local geometry at molybdenum, one can imagine an alternative geometric isomer in which the carbonyl C(4)O(5) and the isocyanide t-BuN(31)C(30) have exchanged positions. This would place the CO in a position anti to the p-tolyl unit, and this is our suggestion for the structure of **13b**. From the ¹H NMR
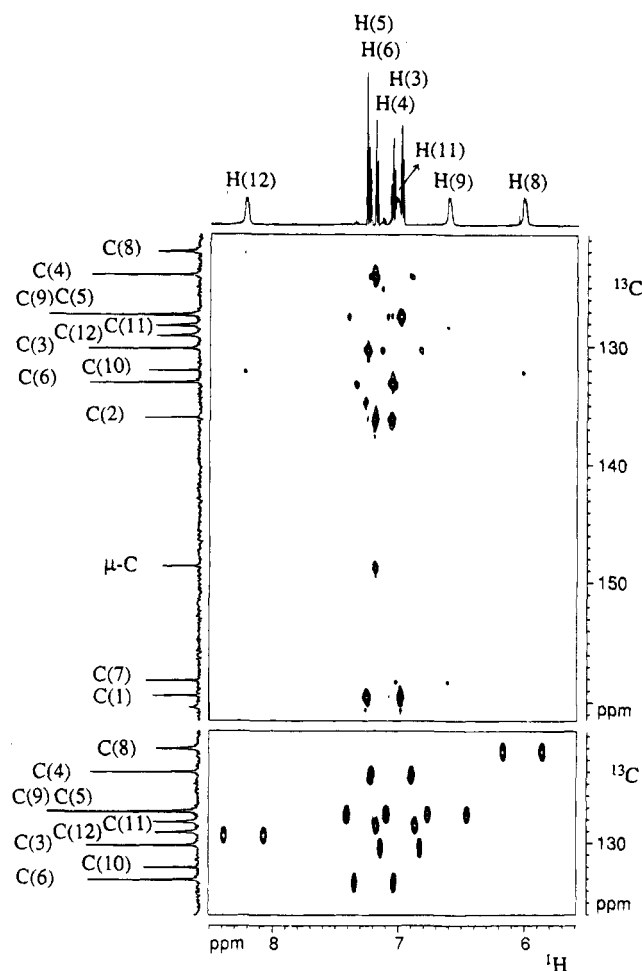
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Figure 5. Section from (a) the *long-range* ¹³C−¹H inverse correlation (upper part) and (b) the *conventional* ¹³C−¹H inverse correlation (lower part) for the Mo complex, **13a**. Note that there are four, broad, p-tolyl protons, and that the μ-C carbon signal (upper trace, lower center) correlates to H(6). The four p-tolyl protons correlate to four *normal* protonated aromatic ¹³C signals, C(8,9) C(11,12), with chemical shifts between 122 and 129 ppm.

of **13b** it may be seen that the signals of the tolyl protons are dramatically shifted as compared to those of **13a**. This could arise because of some steric hindrance between the t-BuNC and the p-tolyl.

Since the solid-state structure for **13a** is known, we measured its ¹H NOESY and ¹³C, ¹H correlations and show the latter in Figure 5. From these spectra it is clear that (1) there are four (definitely broad) p-tolyl proton signals. These four protons exchange pairwise (based on the positive cross-peaks observed in the phase-sensitive NOESY). (2) The four p-tolyl protons correlate to four *normal* protonated aromatic ¹³C signals, with chemical shifts between 122 and 129 ppm. (3) ³J(C,H) can be used to identify all the important quaternary carbons: μ-C(bridging) C(1), C(2), C(7), and C(10). (4) The bridging carbon resonance, at 148.7 ppm, is in the same region as in **1−10**.

From point 2 we conclude that the η²-bond in **13a** has been displaced in that the ¹³C chemical shifts for the aromatic carbons are no longer indicative of complexation, and from point 4 we see that the position of the bridging carbon absorption is not dependent upon the presence of the η²-bond, in keeping with our discussion above. It is interesting that there is still restricted

rotation about the μ-C—C(7) bond. Obviously, the complex is relatively crowded in the region of the *p*-tolyl aromatic moiety; however, based on the proton line widths, the barrier is lower for the Mo complex than for the tungsten complexes, although these complexes are not strictly comparable.

In summary, we conclude that the complexes **1–10** are best thought of as containing an η^2-olefin bond from the *p*-tolyl (or C_5H_7) moiety to the tungsten, with the driving force most likely the desire for an 18-electron configuration. The bridging carbon seems to be a compromise between a carbene and an sp^3 carbon, in that its chemical shift falls between the two expected positions.

Experimental Section

All compounds except **13a** and **13b** were synthesized according to literature procedures.[4]

Synthesis of 13a and 13b. To a stirred solution of [Cp-(CO)(μ-CO)Mo][μ-C(4-tolyl)(dmba)][Pd(I)] (150 mg, 0.25 mmol) in dichloromethane (20 mL) was added *tert*-butyl isocyanide (1 mL) at room temperature. The deep red color of the solution became slightly lighter red and gas evolved. After being stirred for 48 h, the solution was filtered through an alumina column (2 × 5 cm). Elution with pure acetone afforded a red orange band. Evaporating the solvent gave an oily residue which was washed with *n*-hexane (2 × 10 mL) and then redissolved in dichloromethane (10 mL). Addition of *n*-hexane (30 mL) to this solution and cooling at −20 °C afforded, after 24 h, 160 mg (78%) of orange crystals which are a mixture of **13b/13a** in the ratio 3/1. Redissolution of this mixture in dichloromethane layered with *n*-hexane afforded deep red crystals of **13a** (20 mg). All efforts to purify **13b** via fractional crystallization were unsuccessful. Anal. Calcd (Found) for $C_{33}H_{42}IMoN_3OPd$ (MW = 825.98) (+0.25CH_2Cl_2): C, 47.13 (47.11); H, 5.07 (4.77); N, 4.96 (5.02). ^{1}H NMR (CDCl$_3$): **13a**, δ 8.22 (d, 1 H arom, $^3J_{HH}$ = 8.2), 7.22–6.96 (m, 5 H arom), 6.61 (d, 1 H arom, $^3J_{HH}$ = 7.7), 6.01 (d, 1 H arom, $^3J_{HH}$ = 8.2), 4.59 (s, 5 H, Cp), 3.23, 2.64 (AB pattern, 2 H, CH$_2$, $^2J_{HH}$ = 11.5), 2.97, 2.43, 2.15 (3 s, 9 H, NMe$_2$ and 4-Me), 1.57, 1.15 (2s, 18 H, *t*-Bu); **13b**, δ 7.37–6.92 (m, 8H, *p*-tolyl + dmba), 4.74 (s, 5 H, Cp), 3.04 and 2.68 (AB pattern, 2 H, CH$_2$, $^2J_{HH}$ = 11.7), 2.81, 2.31, 2.16 (3 s, 9 H, NMe$_2$ and 4-Me), 1.61, 1.17 (2s, 18 H, *t*-Bu). ^{13}C NMR (CDCl$_3$): **13a**, δ 249.0 (CO), 162.8, 160.4 (*t*-BuNC), 159.3, 158.1, 148.4 (μ-C), 135.9, 133.0, 131.9, 130.0, 129.0, 127.3, 123.9, 121.9 (C arom), 91.7 (Cp), 66.0 (NCH$_2$), 58.2, 57.1 (CMe_3), 52.2, 49.4 (NMe$_2$), 30.8, 30.3 (CMe_3), 20.7 (4-Me); IR (cm^{-1}): ν_{CN} 2150, 2138; ν_{CO} 1797.

X-ray Study of 13a. Intensity data were collected at room temperature on a Philips PW 1100 diffractometer using Mo Kα radiation. Accurate cell dimensions and orientation matrix were obtained from least-squares refinement of the setting angles of 25 well-defined reflections. No decay in the intensities of two standard reflections was observed during the course of data collection. This compound crystallizes in the monoclinic space group *P*2$_1$/*a* with *Z* = 4. Complete crystal data, collection parameters, and other significant details are listed in Table 5. The usual corrections for Lorentz and polarization effects were applied. Computations were performed by using CRYSTALS.[31] Scattering factors and corrections for anomalous dispersion were taken from the literature.[32] The structure was resolved by direct methods (Shelxs 86[33]) and refined by least squares with anisoptropic thermal parameters for all non-

hydrogen atoms. Hydrogen atoms were introduced as fixed contributors in theoretical positions, and their coordinates were recalculated after each refinement. The structure was refined to *R* = 0.048 with the use of 2046 reflections for 362 least-squares parameters.

NMR measurements were performed on CDCl$_3$ solutions (20–30 mg of compound in 0.6 mL of solvent) using a Bruker AMX-500 instrument operating at 500.13, 202.5, 125.8, and 20.8 MHz for ^{1}H, ^{31}P, ^{13}C, and ^{183}W, respectively. Referencing is relative to internal TMS and external 85% H$_3$PO$_4$ for ^{1}H, ^{13}C, and ^{31}P, respectively. Chemical shifts are given relative to WF$_6$ for ^{183}W.

^{183}W–^{1}H Long-Range Correlations. The heteronuclear shift correlation experiments were performed using the HMQC sequence[34] $\pi/2(^1H)-\Delta-\pi/2(^{183}W)-t_1/2-\pi(^1H)-t_1/2-\pi/2(^{183}W)-$acquisition(^{1}H). The defocusing delay Δ was deliberately set to 100 ms, which, given the natural abundance of 14.4% for ^{183}W, allows detection of $^nJ(^{183}W,^1H)$ interactions in the range of 0.5–9.5 Hz with a sensitivity analogous or better than for a corresponding ^{13}C–^{1}H correlation. Absorption mode data in the tungsten dimension were obtained using the TPPI[35] method. Processing involved zero filling and apodization with cosine windows in both dimensions prior to double Fourier transformation, phase correction in ω_1, and magnitude calculation[36] in ω_2. For ^{1}H NOESY, the phase-sensitive NOESY spectra were obtained with a mixing time of 800 ms using standard techniques as described previously.[37]

^{13}C–^{1}H Long-Range Correlations. The heteronuclear shift correlation experiments were performed using the HMQC sequence[34] ^{1}H, 90°$_x$–Δ_1–Δ_2–t_1/2–180°$_x$–t_1/2–Acq(t$_2$); ^{13}C, 90° 90°$_y$ 90°$_x$.

The delays Δ_1 = 1/(2$^1J_{CH}$) and Δ_2 were set to 3.2 and 50 ms, respectively. Processing involved zero filling and apodization with cosine windows in both dimensions prior to double Fourier transformation, absolute value mode representation in ω_1, and magnitude calculation in ω_2.

^{13}C–^{1}H Routine Correlations. The heteronuclear correlation experiments were performed using the HMQC sequence[34] ^{1}H, 90° − Δ − 180° − Δ − 90° − t_1/2 − 180° − t_1/2 − Acq(t$_2$); ^{13}C, 180° 90° 90°.

The delay Δ = 1/(4$^1J_{CH}$) was set to 1.8 ms. The processing parameters are the same used for the ^{183}W–^{1}H long-range correlations.

The following are comments on the individual measurements:

Complex 1. For ^{183}W–^{1}H, there are correlations between tungsten and H-11, H-12, and the Cp protons. The ^{13}C–^{1}H inverse long-range shift correlation shows a weak correlation between the carbonyl resonances at 215.6 ppm and H(8) that supports the η^2-interaction ($^3J_{C-H}$ instead of $^5J_{C-H}$ is the active coupling constant). From the ^{13}C{^{1}H} spectrum the $^1J(^{183}W,^{13}C)$ is 40 Hz for the μ-C.

Complex 2. For ^{183}W–^{1}H, there are correlations between tungsten and H(8), H(9), H(11), H(10), and/or H(11'), and the Cp protons. It is interesting to note that there is correlation of the ^{183}W to one face only of the cyclopentene ring. From the ^{13}C{^{1}H} spectrum, the $^1J(^{183}W,^{13}C)$ values are 166 and 150 Hz for the two CO groups at 212.2 and 221.5 ppm, respectively.

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Complex 3. $^{183}W–^1H$, there are correlations between tungsten and H(11), H(12), and the Cp protons.

Complexes 4 and 7–9. The correlations are as for **3**.

Complex 5. For $^{183}W–^1H$, there are correlations between tungsten and H(9), H(11), CH_3 in the 8 and 12 positions, and the Cp protons.

Complex 6. For $^{183}W–^1H$, there are correlations between tungsten and H(11), H(12), and the Cp protons. The $^{31}P\{^1H\}$ shows a singlet at -13.6 ppm and the satellites due to the tungsten: $^1J(^{183}W,^{31}P) = 17.3$ Hz. From the $^{13}C\{^1H\}$ spectrum the $^1J(^{183}W,^{13}C)$ values are 164 and 165 Hz for the two CO groups at 223.3 and 215.9 ppm, respectively. $^2J(^{13}C,^{31}P)$ for the μ-C is 56.4 Hz.

Complex 10. For $^{183}W–^1H$, there are correlations between tungsten and H(11), H(12), and the Cp protons. From the $^{13}C\{^1H\}$ spectrum the $^1J(^{183}W,^{13}C)$ value is 39 Hz for the μ-C.

Complex 11. For $^{183}W–^1H$, there are correlations between tungsten and H(2), H(4), and the Cp protons. From the $^{13}C\{^1H\}$ spectrum the $^1J(^{183}W,^{13}C)$ values are 204 and 196 Hz for the carbyne ($\delta = 295.9$ ppm) and the CO ($\delta = 220.4$ ppm) carbons, respectively.

Complex 12. The $^{183}W–^1H$ correlation recorded with $\Delta = 150$ ms shows correlations between the tungsten and *all* the protons of the molecule, although several of these are quite weak. Quite surprising is the correlation between the tungsten and the para CH_3 group that occurs via the $^7J(^{183}W,^1H)$ coupling constant.

Complex 13a. The 2-D ^1H NOESY spectrum shows that the protons 8 and 9 are exchanging with 12 and 11, respectively, indicating that there is restricted rotation of the tolyl group. The carbon–proton correlations allow the complete assignment of the resonances and, in particular, show that carbons 7 and 8 fall in the "normal" aromatic range. These facts indicate that there is no η^2-interaction.

Supplementary Material Available: Tables of anisotropic thermal parameters (S1), interatomic distances (S2), and bond angles (S3) for **13a** (3 pages). Ordering information is given on any current masthead page.

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