Bis(alkyne)cycloheptadienyl and Bis(alkyne)σ,η^3-cycloheptenediyl Complexes of Tungsten

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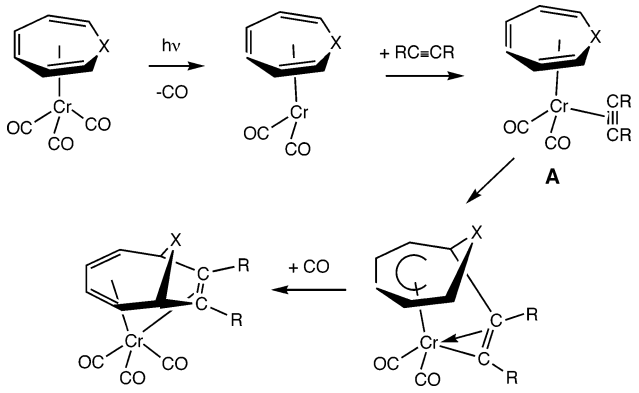
The syntheses of several new bis(alkyne)(carbonyl)(η^5-cycloheptadienyl)tungsten(II) and bis(alkyne)-(carbonyl)(σ,η^3-cycloheptenediyl)tungsten(II) complexes are described. Addition of $HBF_4{\cdot}Et_2O$ to [(η^6-C_7H_8)W(CO)$_3$] (**1**) followed by treatment with diarylalkynes gave the cationic complexes [(η^5-C_7H_9)W(CO)(ArC≡CAr)$_2$][BF_4] (**3a**,**b**; Ar = C_6H_5, 4-MeC_6H_4). These complexes react with nucleophiles $LiHBEt_3$, MeLi, and PhLi to form the neutral σ,η^3-cycloheptenediyl complexes [(σ,η^3-C_7H_9R)W(CO)-(ArC≡CAr)$_2$] (**4a**−**e**; R = H, Me, Ph), which contain η^1, η^2, and η^3 ligands. In all complexes, the two alkyne ligands act as net three-electron donors, although in the neutral complexes the two alkynes are inequivalent. The X-ray structure of [(σ,η^3-C_7H_9Ph)W(CO)(PhC≡CPh)$_2$] (**4e**) is reported. Complexes **4a**,**b** (Ar = C_6H_5, 4-MeC_6H_4, R = H) can be converted back to the cations **3a**,**b** using the triphenylcarbenium ion.

Introduction

We have previously described the [6 + 2] and [5 + 2] cycloaddition reactions of alkynes to η^6-cycloheptatriene and η^5-cyclohexadienyl manifolds respectively coordinated to chromium and manganese.[1−6] These reactions result in the formation of a number of different organic ring products depending upon the transition-metal manifold and the reaction stoichiometry, and Rigby and co-workers have utilized the [6 + 2] process in some elegant syntheses.[7,8] In each case the products are proposed to arise via a series of stepwise insertions of the alkyne into the polyene manifolds. The proposed mechanism for the triene−alkyne [6 + 2] cycloaddition (Scheme 1) involves the photoejection of CO followed by coordination of the alkyne to the metal prior to insertion. A key intermediate is the triene−alkyne species **A** or, in the case of the [5 + 2] additions, a dienyl−alkyne species.

Scheme 1[a]



[a] X = CHR, N-CO_2Et; R = Ar, $SiMe_3$.

Whereas there are many known transition-metal alkyne complexes,[9] examples containing noncyclically conjugated triene or dienyl ligands such as intermediate **A** are rare; indeed we are unaware of any such species prior to this study. We have attempted to isolate such complexes via the reaction of various alkynes with tricarbonyl metal triene or dienyl complexes either thermally or by using UV irradiation at low temperature. In all cases, either cycloaddition products or decomposition was observed. The rationale for using UV light is to displace a carbonyl ligand and generate a 16-electron species that might capture the alkyne substrate. An alternative route to coordinatively unsaturated polyene or polyenyl complexes is protonation of the polyene ring, leading to oxidation at the metal center. One complex that can be protonated in this way is tricarbonyl-(η^6-cycloheptatriene)tungsten(0) (**1**)[10] to give the unsaturated cation **2**. This method has been used to generate many cycloheptadienyl tungsten and molybdenum species with various ancillary ligands.[11,12]

Herein, we report the isolation of cationic cycloheptadienyl alkyne complexes through reaction of **2**, generated in situ from

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(1) Chen, W.; Chaffee, K.; Chung, H.-J.; Sheridan, J. B. *J. Am. Chem. Soc.* **1996**, *118*, 9980−9981.
(2) Chaffee, K.; Huo, P.; Sheridan, J. B.; Barbieri, A.; Aistars, A.; Lalancette, R. A.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 1900−1907.
(3) Chaffee, K.; Sheridan, J. B.; Aistars, A. *Organometallics* **1992**, *11*, 18−19.
(4) Chen, W.; Chung, H.-J.; Wang, C.; Sheridan, J. B.; Cote, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 3337−3344.
(5) Chung, H.-J.; Sheridan, J. B.; Cote, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 4575−4585.
(6) Wang, C.; Sheridan, J. B.; Chung, H.-J.; Cote, M. L.; Lalancette, R. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8966−8972.
(7) Rigby, J. H.; Laxmisha, M. S.; Hudson, A. R.; Heap, C. H.; Heeg, M. J. *J. Org. Chem.* **2004**, *69*, 6751−6760.
(8) Rigby, J. H.; Heap, C. R.; Warshakoon, N. C. *Tetrahedron* **2000**, *56*, 2305−2311.
(9) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.
(10) Salzer, A.; Werner, H. *Z. Anorg. Allg. Chem.* **1975**, *41B*, 88.
(11) Carruthers, K. P.; Helliwell, M.; Hinchliffe, J. R.; de Souza, A.-L. A. B.; Spencer, D. M.; Whiteley, M. W. *J. Organomet. Chem.* **2004**, *689*, 848−859.
(12) Beddoes, R. L.; Hinchliffe, J. R.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1993**, 501−508.

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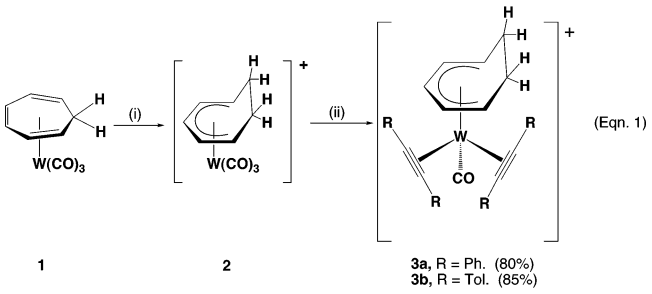
1, with diphenyl- and ditolylacetylene. Each complex contains two alkyne ligands acting as net $3e^-$ donors. These cations react with nucleophiles at C2 of the dienyl ring to form neutral σ,η^3-enediyl bis(alkyne) species that have two inequivalent alkyne ligands that again donate a total of $6e^-$ to the tungsten center.

Results and Discussion

Addition of $HBF_4 \cdot Et_2O$ to tricarbonyl(η^6-cycloheptatriene)-tungsten(0) (**1**) at −78 °C gave the known intermediate **2**. Subsequent addition of excess diphenyl- or ditolylacetylene gave the moderately air stable yellow solids bis(diphenylacetylene)-(carbonyl)(η^5-cycloheptadienyl)tungsten(II) tetrafluoroborate (**3a**) and bis(ditolylacetylene)(carbonyl)(η^5-cycloheptadienyl)tungsten(II) tetrafluoroborate (**3b**), respectively (eq 1). The new complexes are similar to the known cyclopentadienyl species[13] $[CpW(MeC{\equiv}CMe)_2CO]^+$ but have the noncyclically conjugated cycloheptadienyl ligand. To our knowledge, cations **3a** and **3b** are the only examples of noncyclically conjugated diene or dienyl species with alkyne ligands, although such species have been postulated as intermediates in metal-promoted cycloaddition reactions by us and others. In general, the paucity of dienyl−alkyne complexes is due to the facile insertion of alkynes into dienyl or diene ligands; however in this case the third-row metal appears to disfavor insertion and provides a stable alkyne−dienyl species.



Complexes **3a**,**b** were fully characterized by IR and ^1H, ^{13}C, and 2D NMR spectroscopy as well as by elemental analysis. The IR spectrum shows a single carbonyl peak at ν_{max} 2076 cm^{-1}, close to the published value of 2040 cm^{-1} for $[CpW(MeC{\equiv}CMe)_2(CO)][PF_6]$[13] but shifted to higher wavenumber due to the weaker donor diarylalkyne ligands. The ^1H NMR spectrum shows resonances characteristic of symmetric cationic η^5-dienyl groups, suggesting either that the carbonyl lies beneath the methylene carbons or C3 of cycloheptadienyl ligand or that the dienyl group rotates rapidly. The ^{13}C NMR spectrum is also consistent with the assigned structure and shows a single carbonyl at 211.5 ppm and alkyne carbons at 159 and 181.8 ppm. The chemical shift of these latter carbons is consistent with each alkyne being a net three-electron donor to tungsten,[9] giving a formal 18-electron configuration at the metal. Attempts to use other alkynes, phenylacetylene, 2-butyne, and bis-(trimethylsilyl)acetylene, failed to yield tractable products. Likewise, attempts to prepare the analogous molybdenum derivatives from the protonation of tricarbonyl(η^6-cycloheptatriene)molybdenum(0) in the presence of diphenylacetylene also failed to give isolable products.

Reactions with Nucleophiles. The addition of lithium triethylborohydride, methyllithium, or phenyllithium to both **3a**,**b** gave the neutral complexes **4a**−**e** as orange oils in good yield (eq 2). In each case, addition of the nucleophile occurs at C2 of the dienyl manifold to yield the novel σ,η^3-cycloheptenediyl bis(alkyne) complexes that contain η^1, η^2, and η^3 carbon-bound ligands. Complexes **4a**−**e** were fully characterized by IR and ^1H, ^{13}C, and $^1H-^1H$ (2D COSY) NMR spectroscopy as well as by elemental analysis (**4a**,**b**). The neutral complexes contain a carbonyl ligand (ν_{max} 2039 cm^{-1}) and two nonequivalent alkyne ligands. The ^1H NMR spectrum of **4a** has peaks at δ 1.19, 4.04, 4.98, and 6.11 for protons on the σ,η^3-enediyl-coordinated carbons. The ^{13}C NMR spectrum is consistent with the assigned structure and shows a single carbonyl signal (δ 218.7), coordinated alkyne carbons (δ 152.9, 168.1, 177.8, and 183.6), and the σ,η^3-enediyl carbons at 30.2, 73.8, 83.7, and 117.7. The four resonances for the alkyne carbons indicate nonequivalent alkynes, and although the chemical shifts again suggest net three-electron donors, the wide range (153−184 ppm) indicates the different environments of the two ligands.

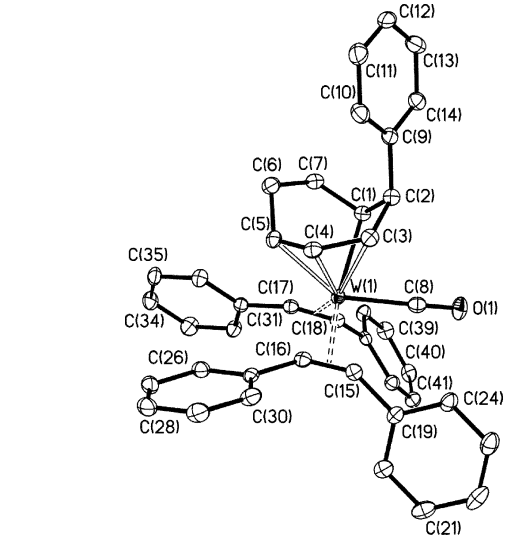
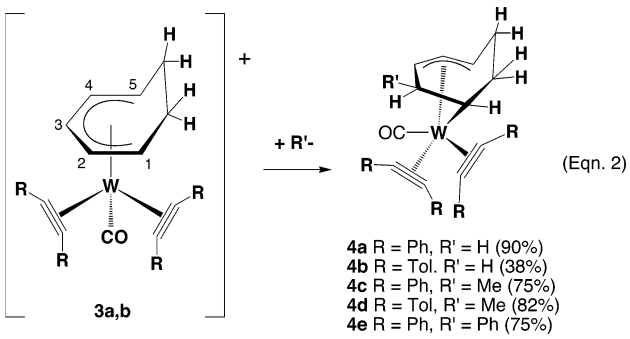


Figure 1. Molecular structure of **4e**·$0.5CH_2Cl_2$ with hydrogen atoms and solvate omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.



The structure of the phenyl adduct **4e** was solved using X-ray crystallography (Figure 1) and shows one alkyne is virtually *trans* to the sigma-bonded C1, whereas the other is *trans* to the allyl group. A closer analysis of the structural data clearly shows the difference between the alkyne ligands, with that *trans* to C1 (C15≡C16) having a slightly shorter bond (1.299(3) Å) and longer W−C distances (av W−C15, W−C16 = 2.125(3) Å) and greater Ph−C≡C bond angles (144°). The second alkyne *trans* to the allyl group has a longer bond (1.315(4) Å), shorter W−C distances (av W−C17, W−C18 = 2.075(3) Å), and smaller Ph−C≡C bond angles (av 139°). Whereas these data do not conclusively show that one alkyne is a 2e donor and the

(13) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698.

other a 4e donor, they do indicate that alkyne C17≡C18 is more tightly bonded to tungsten, most likely a consequence of the weaker *trans* effect of the allyl group compared to the sigma-bonded C1. The allyl group itself shows nonsymmetrical bonding to tungsten with W−C(4) 2.371(3) Å, W−C(5) 2.342-(3) Å, and W−C(3) 2.507(3) Å. The sigma-bonded carbon C1 is 2.253(3) Å from the metal center.

In addition to the major isomers described above, minor isomers were observed for each of the reactions and tentatively identified as rotamers in which the carbonyl ligand lies beneath the methylene carbons C6 and C7 rather than beneath C2. Although not fully characterized, for the reaction of **3a** with phenyllithium, the minor species represented ca. 25% of the isolated product and all the ring proton NMR signals were observable. The general pattern and multiplicity of these signals were similar to those of the major species, suggesting a similar structure. The alternative, in which the nucleophile adds to C1 of the dienyl ring, producing an η^4-cycloheptadiene complex, would be expected to give a significantly different pattern of proton NMR signals and was therefore ruled out. The ^{1}H NMR spectrum of the crystals used in the X-ray study was also measured and showed only one species (the major isomer) was present.

Nucleophilic attack at C2 of dienyl systems is rare, with attack at C1 to give η^4-diene derivatives being the norm. However, isolated examples of C2 attack to generate σ,η^3-enediyl species have been reported[14−16] and with third-row metals[17] and electron-donating ancillary ligands[18] appearing to favor attack at C2. Therefore, the presence of the third-row metal and the electron-rich alkyne ligands in cations **3a**,**b** appears to direct addition to C2 of the cycloheptadienyl ligand and form the σ,η^3-enediyl complexes.

Complexes **4a**,**b** react with triphenylcarbenium hexafluorophosphate or tetrafluoroborate to form the parent cations **3a**,**b** as their PF_6 or BF_4 salts, respectively. Interstingly, the IR and ^{1}H NMR spectral data of **3a**·PF_6 and **3b**·PF_6 are slightly different from their tetrafluoroborate analogues; for example, in **3b**·PF_6 H_3 resonates at 9.03 ppm, whereas in **3b**·BF_4 H_3 is observed at 8.90 ppm. Clearly the counterion has some interaction with the cation; however, crystals could not be obtained for an X-ray study. Complexes **4c**−**e** were also reacted with triphenylcarbenium hexafluorophosphate or triphenylcarbenium tetrafluoroborate but failed to give tractable products presumably due to the fact that a methyl or phenyl group at C2 prevents formation of a conjugated η^5-dienyl group following hydride abstraction.

Conclusions

New bis(alkyne)(carbonyl)(η^5-cycloheptadienyl)tungsten(II) tetrafluoroborate complexes (**3a**,**b**) were formed from tricarbonyl(η^6-cycloheptatriene)tungsten(0) (**1**) and diphenyl- or ditolylacetylene in the presence of HBF_4·Et_2O. These cations contain two three-electron donor alkynes and react with nucleophiles (e.g., hydride, MeLi, or PhLi) at C2 of the dienyl ligand to form neutral σ,η^3-cycloheptenediyl complexes. In contrast to the reactions of alkynes with other dienyl transition-metal manifolds, no coupling or insertion of the alkynes into the metal−dienyl, metal−sigma, or metal−allyl bonds was observed, due perhaps to the stronger metal−alkyne bonds.

Experimental Section

The preparation, purification, and reactions of all complexes described were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques unless otherwise stated. Solvents were dried over Na/benzophenone (THF, Et_2O) and CaH_2 (*n*-hexane, CH_2Cl_2) and were freshly distilled prior to use. NMR spectra were recorded on a Varian Unity Inova (500 MHz) NMR Fourier transform spectrometer. The solvents used for NMR studies were $CDCl_3$ and C_6D_6 as purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Chromatography was performed on silica gel (100−200 mesh, purchased from Sorbent Technologies, Atlanta, GA) or alumina (basic). Filtrations used Celite purchased from Fisher Scientific that was preheated and dried before use. Tricarbonyl(cycloheptatriene)tungsten(0)[19] and ditolylacetylene[20] were prepared via the published procedures.

Bis(diphenylacetylene)(carbonyl)(η^5-cycloheptadienyl)tungsten(II) Tetrafluoroborate (3a). Tetrafluoroboric acid diethyl ether complex (HBF_4·Et_2O) (0.14 mL) was added dropwise to a stirred solution of (η^6-C_7H_8)$W(CO)_3$ (0.20 g, 0.556 mmol) in dichloromethane (10 mL) at −78 °C. After 5 min, the solution was warmed to room temperature and stirred for 30 min. Diphenylacetylene (0.24 g, 1.35 mmol) was added in one portion and the mixture stirred for an additional 30 min under nitrogen. Removal of the solvent under reduced pressure gave an oily residue, which was washed with cold dry ether and recrystallized from CH_2Cl_2/Et_2O (1:5). The product **3a**·BF4 (0.333 g, 80%) was obtained as a solid yellow powder after filtration. **3a**·BF4: ν_{max} (CO)/cm^{-1}, CH_2Cl_2, 2076 (vs). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (t, 1H, H_3), 7.23−7.82 (m, 20H, 4Ph), 5.98(t, 2H, $H_{2,4}$), 4.79 (m, 2H, $H_{1,5}$), 2.80 (m, 2H, $H_{6',7'}$), 2.61 (d, 2H, $H_{6,7}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.5 (CO), 181.8 (*C*≡C), 159.0 (C≡*C*), 142.5, 140.2 (ipso-Ph), 125−133 (4Ph), 121.9 ($C_{2,4}$), 102.1 (C_3), 100.1 ($C_{1,5}$), 34.9 ($C_{6,7}$). Anal. Calcd for $C_{36}H_{29}BF_4OW$; C, 57.75; H, 3.88 (%). Found: C, 58.04; H, 3.84 (%).

Bis(ditolylacetylene)(carbonyl)(η^5-cycloheptadienyl)tungsten-(II) Tetrafluoroborate (3b). Complex **3b** was prepared similarly to **3a** using ditolylacetylene. **3b**·BF_4 (0.473 g, yield 85%): ν_{max} (CO)/cm^{-1}, CH_2Cl_2, 2072 (vs). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (t, 1H, H_3), 7.77 (d, 4H, Ph), 7.37 (d, 8H, 2Ph), 7.19 (d, 4H, Ph), 5.93 (t, 2H, $H_{2,4}$), 4.69 (m, 2H, $H_{1,5}$), 2.79 (m, 2H, $H_{6',7'}$), 2.58 (d, 2H, $H_{6,7}$), 2.48 (s, 6H, 2Me), 2.40 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.8 (CO), 179.1 (*C*≡C), 157.0 (C≡*C*), 142.9, 140.3 (ipso-Ph), 133.0, 130.9, 130.7, 130.0, 129.9, 127.6 (4Ph), 121.6 ($C_{2,4}$), 101.6 (C_3), 97.0 ($C_{1,5}$), 34.5 ($C_{6,7}$), 21.39 (2Me), 21.37 (2Me).

Preparation of 4a. Lithium triethylborohydride (0.5 mL of a 1.0 M solution in THF, 0.5 mmol) was added dropwise to a stirred solution of **3a**·BF_4 (0.333 g, 0.445 mmol) in ether (10 mL) at −78 °C. The solution was slowly warmed to room temperature over 30 min and filtered through Celite, and the filtrate dried under reduced pressure. Chromatography of the residue (silica gel, 30 cm × 2.5 cm), loading (0.5 mL), and eluting with *n*-hexane gave analytically pure **4a** (0.265 g, 90%) as an orange oil after removal of solvent in vacuo. **4a**: ν_{max} (CO)/cm^{-1} (hex), 2044 (vs), (CH_2Cl_2) 2039 (vs). ^{1}H NMR (500 MHz, assignments refer to Figure 1, $CDCl_3$): δ 7.17−7.87 (m, 20H, 4Ph), 6.11 (t, 1H, H_5), 4.98 (t, 1H, H_3), 4.04 (t, 1H, H_4), 2.92 (d, 1H, H_2), 2.31−2.44 (m,4H, $H_{6,6',7,2'}$), 1.19 (m, 1H, H_1), 0.99 (d, 1H, H_7'). ^{13}C NMR (125 MHz, $CDCl_3$): δ 218.7 (CO), 183.6 (*C*≡C), 177.8 (*C'*≡C), 168.1 (C≡*C*), 152.9 (C≡*C'*),

(14) Roell, B. C., Jr.; McDaniel, K. F.; Vaughan, W. S.; Macy, T. S. *Organometallics* **1993**, *12*, 224−228.
(15) Roell, B. C., Jr.; McDaniel, K. F. *J. Am. Chem. Soc.* **1990**, *112*, 9004−9006.
(16) McDaniel, K. F.; Kracker, L. R., II; Thamburaj, P. K. *Tetrahedron Lett.* **1990**, *31*, 2373−2376.
(17) Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Parker, D. G. *J. Organomet. Chem.* **1980**, *194*, C11−C13.
(18) Pearson, A. J.; L., K. S.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060−6074.
(19) King, R. B.; A., F. *Inorg. Chem.* **1966**, *5*, 1837.
(20) Al-Hassan, M. I. *J. Organomet. Chem.* **1990**, *395*, 227−229.

140.6, 140.4, 138.9, 137.4 (ipso-Ph), 127−131 (Ph), 117.5 (C_4), 83.7 (C_3), 73.8 (C_5), 44.1 (C_1), 30.2 (C_2), 28.69 (C_6), 28.65 (C_7). Anal. Calcd for $C_{36}H_{30}OW$: C, 65.26; H, 4.53 (%). Found: C, 65.30; H, 4.70 (%).

Preparation of 4b. Complex **4b** was prepared similarly to **4a** from **3b**·BF_4 (0.38 g, 0.473 mmol) as an analytically pure orange oil (0.178 g, 38%). **4b**: ν_{max} (CO)/cm^{-1} (hex), 2044 (vs), (CH_2Cl_2) 2036 (vs). ^{1}H NMR (500 MHz, assignments refer to Figure 1, $CDCl_3$): δ 7.2−7.8 (m, 16H, 4Ar), 6.09 (t, 1H, H_5), 4.94 (t, 1H, H_3), 3.97 (t, 1H, H_4), 2.89 (d, 1H, H_2), 2.2−2.5 (m, 16H, 4Me, $H_{6,6',7,2'}$), 1.16 (m, 1H, H_1), 0.89 (d, 1H, $H_{7'}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 219.7 (CO), 182.3 (*C*≡C), 176.8 (*C*′≡C), 167.3 (C≡*C*), 152.2 (C≡*C*′), 133−138 (ipso-Ar), 125−131 (Ar), 117.5 (C_4), 83.2 (C_3), 73.2 (C_5), 44.0 (C_1), 30.1 (C_2), 28.7 (C_6), 28.2 (C_7), 21.44 (Me), 21.34 (Me), 21.25 (Me), 21.19 (Me). Anal. Calcd for $C_{40}H_{38}OW$: C, 66.87; H, 5.29 (%). Found: C, 66.99; H, 5.40 (%).

Preparation of 4c. Methyllithium (0.56 mL of a 1.0 M solution in THF, 0.56 mmol) was added dropwise to a stirred solution of **3a**·BF_4 (0.400 g, 0.535 mmol) in ether (20 mL) at −78 °C. The solution was slowly warmed to room temperature over 30 min and filtered through Celite, and the filtrate dried under reduced pressure. Chromatography of the residue (silica gel, 30 cm × 2.5 cm), loading (0.5 mL), and eluting with *n*-hexane gave **4c** (0.27 g, 75%) as a yellow oil after removal of solvent in vacuo. The product is a mixture of two isomers in a 4:1 ratio; only the major isomer was fully characterized. **4c-major**: ν_{max} (CO)/cm^{-1} (hex), 2045 (vs), (CH_2Cl_2) 2039 (vs). ^{1}H NMR (500 MHz, assignments refer to Figure 1, $CDCl_3$): δ 7.21−7.85 (m, 20H, 4Ph), 6.08 (t, 1H, H_5), 4.97 (dd, 1H, *J*(HH) = 6.5 Hz, H_3), 4.26 (dd, 1H, *J*(HH) = 6.5 Hz, H_4), 2.62 (d, 1H, H_2), 2.45 (m, 2H, $H_{6,7}$), 2.23 (m, 1H, $H_{6'}$), 0.97 (m, 2H, $H_{7',1}$), 0.51 (d, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 218.3 (CO), 181.2 (*C*≡C), 175.8 (*C*′≡C), 166.2 (C≡*C*), 152.2 (C≡*C*′), 126.9−140.3 (Ph), 117.5 (C_4), 90.3 (C_3), 74.7 (C_5), 36.4 (C_1), 36.2 (C_2), 35.5 (C_6), 31.7 (C_7), 25.6 (Me).

Preparation of 4d. Complex **4d** was prepared similarly to **4c** from **3b**·BF_4 (0.400 g, 0.498 mmol) as a yellow oil (0.30 g, 82%). The product is a mixture of two isomers in a 7:1 ratio; only the major isomer was fully characterized. **4d-major**: ν_{max} (CO)/cm^{-1} (Et_2O), 2038 (vs). ^{1}H NMR (500 MHz, assignments refer to Figure 1, $CDCl_3$): δ 7.0−7.9 (m, 16H, 4Ar), 6.03 (t, 1H, H_5), 4.92 (dd, 1H, *J*(HH) = 6.0 Hz, H_3), 4.19 (dd, 1H, *J*(HH) = 6.0 Hz, H_4), 2.62 (m, 1H, H_2), 2.3−2.5 (m, 14H, 4Me, $H_{6'7}$), 2.20 (m, 1H, $H_{6'}$), 0.91 (m, 2H, $H_{6',1}$), 0.49 (d, 3H, *J*(HH) = 5.3 Hz, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 218.0 (CO), 180.0 (*C*≡C), 174.7 (*C*′≡C), 165.4 (C≡*C*), 151.5 (C≡*C*′), 134−139 (ipso-Ar), 126−130 (Ar), 117.4 (C_4), 89.9 (C_3), 74.3 (C_5), 36.4 (C_1), 36.0 (C_2), 35.5 (C_6), 31.6 (C_7), 25.6 (Me), 21.1−21.4 (4Me).

Preparation of 4e. Phenyllithium (0.11 mL of a 2.0 M solution in THF, 0.22 mmol) was added dropwise to a stirred solution of **3a**·BF_4 (0.146 g, 0.195 mmol) in ether (20 mL) at −78 °C. The solution was slowly warmed to room temperature over 30 min and filtered through Celite, and the filtrate dried under reduced pressure. Chromatography of the residue (alumina, 30 cm × 2.5 cm), loading with hexane (0.5 mL), and eluting with *n*-hexane/THF (94:4) gave **4e** (0.27 g, yield 75%) as a yellow powder after removal of solvent in vacuo. The product is a mixture of two isomers in a 3:1 ratio. Yellow crystals of **4e**·0.5CH_2Cl_2 used in the X-ray study were grown from a hexane/dichloromethane solution at −10 °C over a few days. **4e-major**: ν_{max} (CO)/cm^{-1} (hex), 2041 (vs). ^{1}H NMR (500 MHz, assignments refer to Figure 1, $CDCl_3$): δ 7.85−6.94 (m, 25H, 5Ph), 6.20 (t, 1H, H_5), 4.87 (t, 1H, H_3), 4.70 (t, 1H, H_4), 3.90 (m, 1H, H_2), 2.06 (m, 1H, H_6), 1.85 (m, 1H, H_7), 1.63 (m, 1H, $H_{6'}$), 1.45 (d, 1H, H_1), 0.85 (m, 1H, $H_{7'}$). ^{13}C NMR (125 MHz, C_6D_6): δ 218.4 (CO), 181.2 (*C*≡C), 175.6 (*C*′≡C), 166.2 (C≡*C*), 153.0 (C≡*C*′), 148.1 (ipso-Ph attached to C_5), 140.7, 140.4, 138.8, 137.6 (ipso-Ph), 125.6−130.1 (Ph), 119.6 (C_4), 81.3 (C_3), 77.1 (C_5), 45.7 (C_2), 38.4 (C_1), 36.2 (C_6), 29.4 (C_7). **4e-minor**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85−6.94 (m, Ph), 6.50 (t, 1H), 5.58 (dd, 1H), 3.80 (dd, 1H), 3.29 (dd, 1H), 1.95 (m, 1H), 1.77 (m, 3H), 0.60 (d, 1H).

Preparation of 3b·PF_6 from 4b. Triphenylcarbenium hexafluorophosphate ([Ph_3C]PF_6) (32 mg, 0.083 mmol) was added in one portion to a solution of **4b** (60 mg, 0.084 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction was stirred for 10 min at 0 °C and warmed to room temperature over 30 min. Removal of the solvent in vacuo until 0.5 mL of solution remained and precipitation with ether (10 mL) gave the solid yellow product **3b**·PF_6 (60 mg, 76%), which was washed with cold dry ether (2 × 3 mL) and dried under vacuum. Analytically pure product was obtained by precipitation from CH_2Cl_2 solution using ether. **3b**·PF_6: ν_{max} (CO)/cm^{-1}, (CH_2Cl_2) 2069 (vs). **3b**·PF_6.CH_2Cl_2: Anal. Calcd for $C_{41}H_{39}Cl_2PF_6OW$: C, 51.96; H, 4.12. Found: C, 51.89; H, 4.23. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.90 (t, 1H, H_3), 7.71 (d, 4H, Ph), 7.35 (d, 8H, 2Ph), 7.17 (d, 4H, Ph), 5.88 (dd, 2H, $H_{2,4}$), 4.67 (d, 2H, $H_{1,5}$), 2.77 (d, 2H, $H_{6',7'}$), 2.57 (m, 2H, $H_{6,7}$), 2.45 (s, 6H, 2Me), 2.38 (s, 6H, 2Me).

3a·PF_6 was prepared similarly from **4a** in 82% yield.

X-ray crystallographic Study. Data were collected on a Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation and were measured using a combination of ϕ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package.[21] The structure was solved and refined using SHELXTL V6.1[22] for full-matrix least-squares refinement that was based on F^2. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom.

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Supporting Information Available: Crystallographic data for **4e** in cif format are available free of charge via the Internet at http://pubs.acs.org.

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(21) Otwinowski, Z.; Minor, W. In *Methods in Enzymology, Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: London, 1997; Vol. 276, pp 307−326.

(22) Sheldrick, G. M. *SHELXTL/PC*, Version 6.1 Windows NT Version; Bruker AXS Inc.: Madison, WI, 2001.