The product was isolated by adding the solution dropwise to ether (20 mL), decanting the solvent, rinsing the residue by decantation with ether, and recrystallizing from freshly distilled acetonitrile and ether (432 mg, 91% yield): IR (Nujol) 2133, 2097, 2086, 1762 cm^{-1}; ^1H NMR (CD_3CN, 0 °C) δ 2.19 (3 H, s), 4.47 (1 H, d, J = 7.6 Hz), 5.19 (1 H, s), 5.98 (1 H, dd, J = 7.6, 5.9 Hz), 6.56 (1 H, d, J = 6.1 Hz), 7.15 (1 H, dd, J = 6.1, 5.9 Hz). This compound was extremely moisture sensitive, and satisfactory combustion analysis was not obtained.

Tricarbonyl[6-acetoxy-5-hydroxy-1-(trifluoromethyl)-cyclohexadiene]iron (9). The dienyl salt (8) (100 mg, 0.205 mmol) was dissolved in acetonitrile (2 mL) at 0 °C. This was added dropwise, with stirring to water, buffered with $NaHCO_3$ (1.5 mL), and the mixture was allowed to warm to room temperature. Ether extraction in the usual way, followed by purification by flash chromatography (1:1 ethyl acetate/hexane, R_f = 0.4), gave yellow crystals (69 mg, 83% yield): mp 100–101 °C; $[\alpha]^{23}_D$ −47.0° (c 0.65); IR 3363, 2073, 2006, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (3 H, s), 3.16 (2 H, m becomes 1 H, dd J = 5.2, 3.7 Hz after D_2O shake), 3.92 (1 H, d, J = 3.8 Hz), 4.40 (1 H, s), 5.50 (1 H, t, J = 5.4 Hz), 5.82 (1 H, dq, J = 5.3, J_F = 0.7 Hz). Anal. Calcd for $C_{12}H_9F_3FeO_6$: C, 39.78; H, 2.51. Found: C, 39.85; H, 2.73.

Tricarbonyl[dimethyl [2-5-η-6-acetoxy-5-(trifluoromethyl)cyclohexa-2,4-dienyl]malonate]iron (10). Sodium hydride (64 mg of 50% dispersion in mineral oil) was rinsed with hexane and THF at 0 °C. Tetrahydrofuran (4 mL) and dimethyl malonate (200 mg) were added, and the mixture was stirred for 15 min. A 1-mL aliquot of this solution was added via syringe to a stirred suspension of 8 (100 mg, 0.206 mmol). The mixture was stirred at room temperature for 30 min, water (2 mL) was added, and the product was extracted with ether in the usual way. Chromatography on silica gel (25% ether in hexane, R_f = 0.1) afforded 10 as a yellow oil (89 mg, 94% yield): $[\alpha]^{23}_D$ −93.0° (c 1.12); IR 2073, 2013, 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (3 H, s), 2.60 (1 H, m), 3.30 (1 H, ddd, J = 5.5, 3.6, 1.8 Hz), 3.74 (3 H, s), 3.76 (3 H, s), 3.80 (1 H, d, J = 5.5 Hz, obscured), 4.97 (1 H, d, J = 1.8 Hz), 5.30 (1 H, dd, J = 5.5, 4.5 Hz) 5.63 (1 H, dq, J = 4.5, J_F = 0.7 Hz); ^{13}C NMR ($CDCl_3$) δ 207.9, 169.8, 168.2, 168.0, 125.9 (q, J_F = 270 Hz, CF_3), 83.9, 83.2, 70.8, 59.1, 58.9, 55.6, 52.7, 49.0, 47.9, 20.8.

Crystal Data for Compound 4: $C_{10}H_7FeF_3O_5$, monoclinic, space group $P2_1$ (No. 4), a = 6.915 (1) Å, b = 7.889 (1) Å, c = 10.891 (2) Å, β = 95.44 (1)°, V = 591.5 Å^3. For Z = 2 and fw = 320.01 the calculated density is 1.80 g/cm^3. Using an Enraf-Nonius CAD4 diffractometer, Mo Kα (λ = 0.709 30 Å) radiation, a total of 2529 reflections were collected, of which 2333 were unique. The structure was solved by direct methods. A total of nine atoms were located from the first E-map and the remaining atoms found in succeeding difference Fourier syntheses. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares on F (R factor 0.030). The absolute configuration was confirmed by the R factor test (R(enantiomer) = 0.041). Atomic coordinates, bond lengths and angles, and thermal parameters are available as supplementary material.

Acknowledgment. We are grateful to the National Science Foundation for financial support (Grant CHE 8921944 and Research Experience for Undergraduates Grant CHE 8804605) and to Dr. R. J. Pryce of Shell Research (U.K.) Ltd., for generous gifts of (trifluoromethyl)cyclohexadienediol (3).

Registry No. 3, 131101-28-5; 4, 138061-94-6; 5, 138061-95-7; 6, 138061-96-8; 7, 138061-98-0; 8, 138062-00-7; 9, 138062-01-8; 10, 138062-02-9; nonacarbonyldiiron, 15321-51-4; dimethyl malonate, 108-59-8.

Supplementary Material Available: Complete structural report for complex 4 including tables of positional and thermal parameters, general temperature factor expressions, bond distances, bond angles, and intensity data (11 pages). Ordering information is given on any current masthead page.

Functionalization of Metalated Cyclopentadienyl Ligands via Palladium-Catalyzed Cross-Coupling Reactions

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Received June 19, 1991

The palladium-catalyzed coupling reaction between tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and various alkynyl-, aryl-, and vinylstannanes yields the corresponding coupled derivatives. The three classes of tin coupling partners were represented by (2-phenyl-1-ethynyl)trimethylstannane, 1-propynyltrimethylstannane, and 1-hexynyltri-*n*-butylstannane; phenyltri-*n*-butylstannane, and (4-methylphenyl)trimethylstannane; and (*Z*)-methyl 3-(tributylstannyl)acrylate, trimethylvinylstannane, and [2-(trimethylsilyl)-1(*E*)-ethenyl]trimethylstannane. This chemistry demonstrates a new, general route for the formation of a variety of functionally substituted η^5-cyclopentadienyl transition-metal compounds, whereby the cyclopentadienyl ring can be derivatized by several classes of organostannane reagents without affecting the other ligands on the transition metal.

Introduction

There are few general routes in the literature for the functionalization of metalated η^5-cyclopentadienyl half-sandwich complexes. Historically much study has been directed in this area due to certain aromatic-type electrophilic substitutions demonstrated by ferrocene. The products resulting from substitution on ferrocene often have unique chemical and physical properties.[1] Despite the successes of the ferrocene-based cases, few other η^5-cyclopentadienyl transition-metal complexes have undergone similar aromatic-type substitutions. The reason that most η^5-cyclopentadienyl metal complexes fail to undergo ring substitution is perhaps their inherent lack of aromatic character, or even more reasonable, more facile

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† Deceased, July 19, 1989.

(1) (a) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196. (b) Wright, M. E. *Organometallics* **1990**, *9*, 853.

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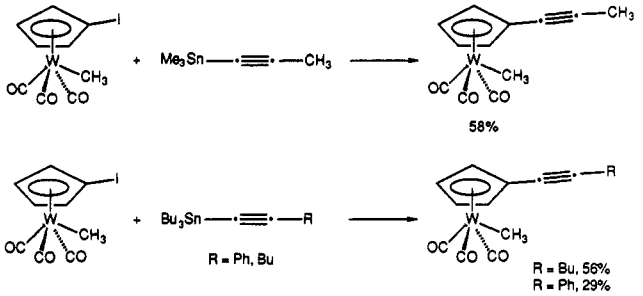
Scheme I



reaction pathways that can occur under the reaction conditions.[1] Regardless, η^5-cyclopentadienyl metal compounds have shown an inability to form functionally substituted derivatives by ring-substitution routes, and this has severely limited the progress of η^5-cyclopentadienyl metal half-sandwich chemistry.[1] A potential way to overcome the difficulties associated with ring substitution on metalated η^5-cyclopentadienyl complexes takes advantage of the palladium-catalyzed cross-coupling reactions reported earlier from these laboratories.[2]

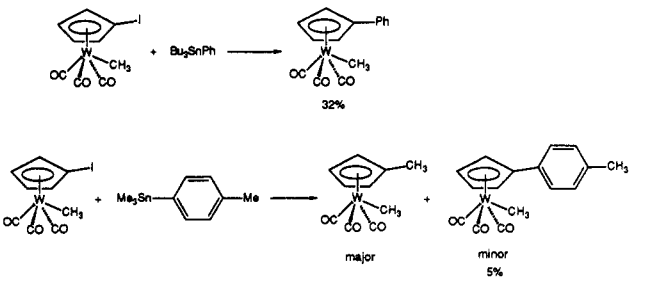
It has been shown earlier,[3,4] that many iodo-η^5-cyclopentadienyl transition metal complexes are easily prepared. These represent one of the coupling partners in the palladium-catalyzed cross-coupling reaction. With the wide variety of tin reagents available, a plethora of potential permutations exist pairing up various iodo-η^5-cyclopentadienyl transition metal complexes with the numerous tin reactions. The multitude of promising coupled products, thus functionalizing metalated cyclopentadienyl rings, is vast indeed. In order to demonstrate the utility of this chemistry, a variety of coupling reactions have been performed in three classes: alkynyl, vinyl, and aryl couplings.

Results and Discussion

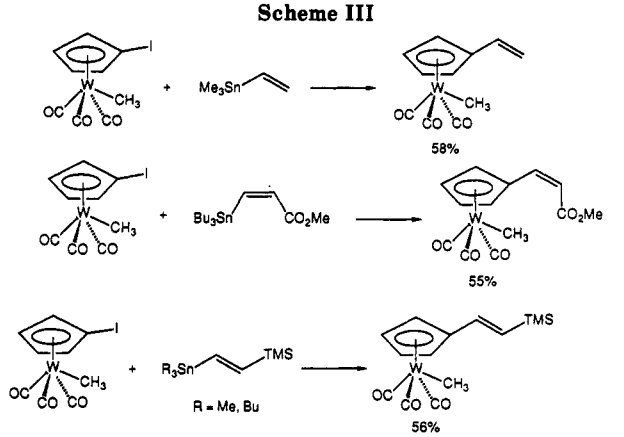
Alkynyl Couplings. Initially, the tricarbonyl(1-propynyl-η^5-cyclopentadienyl)methyltungsten was prepared via an alkynylpalladium-catalyzed tin coupling. With this reaction serving as precedence, we explored several more alkynyl coupling reactions. Due to the stability and ease of preparation, the iodoalkyl partner was restricted to tricarbonyl(iodo-η^5-cyclopentadienyl)-methyltungsten. Using (phenylethynyl)tributylstannane, the tricarbonyl[(phenylethynyl)-η^5-cyclopentadienyl]-methyltungsten was synthesized, which is analogous to the iron compound prepared previously, except that in this case the butyltin reagent was used. Also, using the 1-hexynyltributylstannane, the tricarbonyl(1-hexynyl-η^5-cyclopentadienyl)methyltungsten was prepared. Moreover, it had been shown previously[3,4] that, by using octacarbonyldicobalt, these types of alkynes can easily be "butterfly" protected, thus introducing another metal into the complex. The reactions that represent the tungsten–alkynyl couplings are shown in Scheme I.

Aryl Couplings. In addition to the alkynyl coupling reactions, we explored palladium-catalyzed couplings using aryl tin reagents. Using phenyltributylstannane (or the analogous trimethylstannane), the phenyl-coupled product can be synthesized. Using the *p*-tolyltrimethylstannane, the desired coupled product was also prepared, namely tricarbonyl(4-tolyl-η^5-cyclopentadienyl)methyltungsten. Unfortunately, the major product, as seen by ^{1}H NMR, is the methyl-coupled product. This suggests that the

Scheme II



Scheme III



methyl group on the tin reagent transmetalates to palladium slightly better than the *p*-tolyl group. While the yield of the desired product is low, the coupled product is seen and easily characterized. While methyltin reagents generally give greater yields of the coupled products than their butyl analogues, the yield of the *p*-tolyl-coupled product could possibly be increased by using the analogous butyltin reagent, since the migration of the butyl group would not be expected to compete with the transfer of the *p*-tolyl group. Thus, the compounds representing aryl couplings are shown in Scheme II.

Vinyl Couplings. In order to demonstrate that these couplings could be applied to vinylstananes, couplings were employed to elaborate the cyclopentadienyl ring in the tungsten-based system. The vinyl coupling using the trimethylvinylstannane and the tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten generated the desired product, namely tricarbonyl(1-ethenyl-η^5-cyclopentadienyl)methyltungsten in good yield. One useful feature of the palladium-catalyzed coupling reaction is the retention of stereochemistry in tin reagent. To test this in the tungsten-based system, the coupling between (*Z*)-methyl 3-(tributylstannyl)acrylate and the tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten was performed. Indeed, the product was formed in good yield with no isomerization of the double bond. Further proof was demonstrated by the coupling using [2-(trimethylsilyl)-1(*E*)-ethenyl]tributylstannane. Here again, the coupled product was generated in good yield with preservation of the double-bond geometry. In addition, these reactions demonstrate that functionality on the vinyltin reagent may be tolerated; the ester group and the trimethylsilyl group are undisturbed in the coupling reaction. Hence, the compounds that represent vinylic type couplings are shown in Scheme III.

Summary

The palladium-catalyzed coupling reaction has been used to demonstrate that a variety of organostannanes can be used to derivatize metalated cyclopentadienyl rings.

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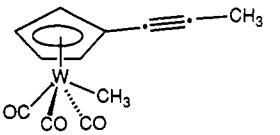
This process has the additional advantage of not affecting the other ligands on the transition-metal fragment, thus suggesting that modification of the cyclopentadienyl ligand can be accomplished selectively by several classes of functional groups. Since the palladium-catalyzed coupling tolerates a wide variety of functionality on both the alkyl halide and the organostannane, the possible combinations arising from these couplings are considerable. In addition, this tolerance of functionality eliminates the need for protection–deprotection steps required by traditional synthetic methodology. Furthermore, in the case of alkynyl-coupled products, the triple bond can be butterfly protected with known cobalt chemistry[3,4] to introduce another transition metal into these complexes. Also, for couplings using vinyl organostannanes, the geometry of the double bond is preserved. These results, therefore, represent a potentially new and general route to the formation of a variety of substituted η^5-cyclopentadienyl transition metal compounds.

Experimental Section

General Procedures. All manipulations were carried out under a protective atmosphere of argon in carefully dried equipment. Conventional vacuum line and/or Schlenk techniques were used. Liquids were transferred by syringe or cannula. Infrared spectra were recorded on a Beckman 4240 grating infrared spectrometer or on a Perkin-Elmer 1600 FTIR, recorded in the Fourier transform mode. Abbreviations: v, very; s, strong; w, weak; m, medium. The ^{1}H NMR spectra and the broad-band proton-decoupled ^{13}C NMR spectra were recorded in the Fourier transform mode on a Bruker AC300P spectrometer operating at 300 MHz for proton and at 75 MHz for carbon. The NMR chemical shifts are reported (ppm) vs Me_4Si by assigning the ^{1}H impurity in the solvent ($CDCl_3$) at δ 7.24. The ^{13}C chemical shifts are reported relative to the ^{13}C triplet ($CDCl_3$) at δ 77.00. Elemental analyses were carried out by Atlantic Microlab, Norcross, GA. High-resolution mass spectra (HRMS) were obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska, Lincoln, NE. Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected.

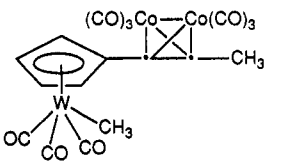
Materials. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen from sodium–benzophenone ketyl. *sec*-Butyllithium was obtained from Aldrich as a 1.3 M solution in cyclohexane. The molarity of the lithium reagents was checked periodically by titration with 2,5-dimethoxybenzyl alcohol[5] in benzene. The following compounds were used as received: dicarbonylcyclopentadienyliron dimer (Aldrich), hexacarbonylmolybdenum (Aldrich), octacarbonyldicobalt (Strem), hexacarbonyltungsten (Aldrich), cerium trichloride (Aldrich), methylphenylacetylene (Farchan). The following compounds were prepared by known methods: tricarbonyl(η^5-cyclopentadienyl)methyltungsten,[6] tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten,[4] bis(acetonitrile)palladium dichloride,[7] (phenylethynyl)trimethylstannane,[8-11] 1-propynyltrimethylstannane,[12] 1-hexynyltributylstannane,[8,13] trimethylphenylstannane,[14] tributylphenylstannane,[14] (4-methylphenyl)trimethylstannane,[15] [1(*E*)-(methoxycarbonyl)ethenyl]tributylstannane,[16,17] [2-(trimethylsilyl)-1(*E*)-ethenyl]trimethylstannane,[16] [2-(trimethylsilyl)-1(*E*)-ethenyl]tributylstannane,[18] trimethylvinylstannane,[19] phenylmethylacetylene, hexacarbonyldicobalt.[20] Purification of 1,2-diiodoethane[21] was achieved by washing with saturated sodium thiosulfate until the washings were clear, extracting the aqueous layer with ether, and removing the ether by rotary evaporation to give a white solid.

Preparations. Preparation of Tricarbonyl(1-propynyl-η^5-cyclopentadienyl)methyltungsten.



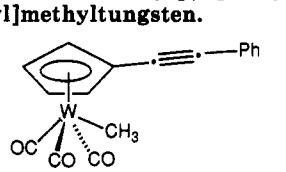
To a solution of 0.474 g (1.00 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.203 g (1.00 mmol) of trimethylpropynylstannane in 5 mL of DMF was added 0.0052 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 10 h at room temperature. The reaction mixture was quenched with water, extracted with ether (3 × 50 mL), and dried ($MgSO_4$). Flash chromatography on silica, eluting with hexane, gave the desired product as a yellow solid (58%): IR (Nujol) ν 2240.2 (w), 2016.7 (vs), 1926.6 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.42–5.44 (m, 2 H), 5.19–5.21 (m, 2 H), 1.99 (s, 3 H), 0.501 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 228.52, 215.54, 95.51, 93.98, 88.24, 87.97, 70.77, 4.023, -27.63; HRMS exact mass for $C_{12}H_{10}O_3{}^{184}W$, calcd m/z 386.0140, found 386.0141.

Preparation of Tricarbonyl(1-propynyl-η^5-cyclopentadienyl)methyltungsten–Hexacarbonyldicobalt Complex.



To a solution of 0.386 g (1.00 mmol) of tricarbonyl(1-propynyl-η^5-cyclopentadienyl)methyltungsten in 20 mL of benzene was added via cannula 0.376 g (1.10 mmol) of octacarbonyldicobalt, previously weighed out in the drybox, in 10 mL of benzene. The solution was stirred for 1 h under argon. The solvent was removed by rotary evaporation, and the product was chromatographed (flash, silica) eluting with hexane. The hexane was removed by rotary evaporation to afford 0.355 g (53%) of a purple solid: IR (Nujol) ν 2091.6, 2054.7, 2027.6, 1927.5 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.48 (m, 2 H), 5.39 (m, 2 H), 2.73 (s, 3 H), 0.519 (s, 3 H). Anal. Calcd for $C_{18}H_{10}O_9Co_2W$: C, 32.17; H, 1.499. Found: C, 32.30; H, 1.54.

Preparation of Tricarbonyl[(2-phenyl-1-ethynyl)-η^5-cyclopentadienyl]methyltungsten.



To a solution of 0.273 g (0.500 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.158 g (0.600 mmol) of (2-phenyl-1-ethynyl)trimethylstannane in 5 mL of DMF was added 0.0026 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with water, buffered at pH 8, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on silica eluting with hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.128 g (29%) of the desried product as a yellow oil: IR (neat) ν 3112.4 (m), 2968.8

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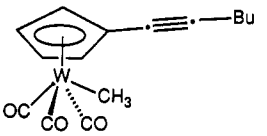
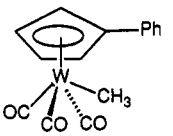
(m), 2900.4 (m), 2232.1 (w), 2012.7 (vs), 1907.8 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30–7.48 (m, 5 H), 5.57–5.58 (m, 2 H), 5.29–5.31 (m, 2 H), 0.576 (s, 3 H, J_{W-H} = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ 228.19, 215.22, 131.87, 128.93, 128.40, 121.98, 94.27, 91.13, 88.63, 80.54, -27.68. Anal. Calcd for $C_{17}H_{12}O_3W$: C, 45.87; H, 2.72. Found: C, 45.74; H, 2.78.

Preparation of Tricarbonyl(1-hexynyl-η^5-cyclopentadienyl)methyltungsten.



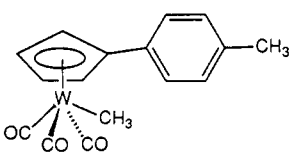
To a solution of 0.237 g (0.500 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.220 g (0.600 mmol) of 1-hexynyltributylstannane in 10 mL of DMF was added 0.0026 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 4 h at room temperature. The reaction mixture was quenched with water, buffered at pH 8, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on silica eluting with 20:1 hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.240 g (56%) of the desired product as a yellow oil: IR (neat) ν 2957.9 (m), 2930.4 (m), 2871.4 (m), 2241.1 (w), 2014.4 (vs), 1916.0 (vs); ^1H NMR ($CDCl_3$) δ 5.42–5.54 (t, 2 H), 5.19–5.21 (t, 2 H), 2.30–2.35 (t, 2 H), 1.42–1.53 (m, 4 H), 0.881–0.929 (t, 3 H), 0.496 (s, 3 H, J_{W-H} = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ 228.60, 215.58, 95.68, 94.05, 92.94, 87.82, 71.58, 30.74, 21.89, 18.80, 13.52, -27.37; HRMS exact mass for $C_{15}H_{16}O_3{}^{184}W$, calcd m/z 428.0610, found 428.0610. Anal. Calcd for $C_{15}H_{16}O_3W$: C, 42.08; H, 3.77. Found: C, 41.81; H, 3.78.

Preparation of Tricarbonyl(1-phenyl-η^5-cyclopentadienyl)methyltungsten.



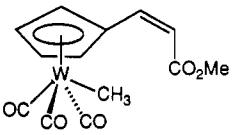
To a solution of 0.237 g (0.500 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.220 g (0.600 mmol) of phenyltri-*n*-butylstannane in 10 mL of DMF was added 0.0026 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 72 h at room temperature. The reaction mixture was quenched with water, buffered at pH 8, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on silica eluting with 10:1 hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.067 g (32%) of the desired product as a yellow oil: IR (neat) ν 2961.6 (w), 2916.7 (w), 2849.4 (w), 2017.0 (vs), 1919.5 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.75 (m, 5 H), 5.76–5.79 (t, 2 H), 5.54–5.56 (t, 2 H), 0.445 (s, 3 H, J_{W-H} = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 218.29, 213.54, 137.78, 132.54, 128.64, 128.02, 93.83, 93.63, -31.44; HRMS exact mass for $C_{15}H_{12}O_3{}^{184}W$, calcd m/z 424.0296, found 424.0281.

Preparation of Tricarbonyl[1-(4-methylphenyl)-η^5-cyclopentadienyl]methyltungsten.



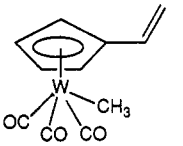
To a solution of 0.237 g (0.500 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.153 g (0.600 mmol) of (4-methylphenyl)trimethylstannane in 10 mL of DMF was added 0.0026 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with water, buffered at pH 8, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the sovlent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on silica eluting with 10:1 hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.011 g (5%) of the desired product as a yellow oil: IR (neat) ν 2003.9 (vs), 1908.1 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13–7.23 (m, 4 H), 5.70–5.72 (t, 2 H), 5.34–5.36 (t, 2 H), 2.33 (s, 3 H), 0.225 (s, 3 H, J_{W-H} = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ 229.24, 216.34, 138.49, 129.49, 125.84, 113.49, 88.80, 88.40, 62.99, 21.19, -28.97; HRMS exact mass for $C_{16}H_{14}O_3{}^{184}W$, calcd m/z 438.0453, found 438.0443. Anal. Calcd for $C_{16}H_{14}O_3W$: C, 43.86, H, 3.22. Found: C, 44.51; H, 3.58.

Preparation of Tricarbonyl[[(methoxycarbonyl)-1(*E*)-ethenyl]-η^5-cyclopentadienyl]methyltungsten.



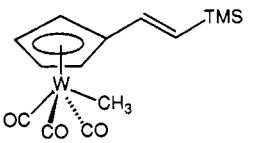
To a solution of 0.237 g (0.500 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.225 g (0.600 mmol) of (*Z*)-methyl 3-(tributylstannyl)acrylate in 10 mL of DMF was added 0.0026 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with water, buffered at pH 8, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on alumina eluting with 10:1 hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.119 g (55%) of the desired product as a yellow oil: IR (neat) ν 3141.8 (w), 2952.6 (m), 2902.4 (m), 2011.3 (vs), 1904.6 (vs), 1721.4 (s), 1637.4 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.37, 6.42 (d, 1 H, J_{H-H} = 12.6 Hz), 5.94–5.96 (t, 2 H), 5.77, 5.82 (d, 1 H, J_{H-H} = 12.6 Hz), 3.72 (s, 3 H), 0.406 (s, 3 H, J_{W-H} = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 228.00, 215.41, 165.89, 135.64, 118.39, 101.83, 94.55, 91.77, 51.50, -31.77. Anal. Calcd for $C_{13}H_{12}O_5W$: C, 36.14; H, 2.80. Found: C, 36.67; H, 2.91.

Preparation of Tricarbonyl(1-ethenyl-η^5-cyclopentadienyl)methyltungsten.



To a solution of 0.474 g (1.00 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.191 g (1.00 mmol) of trimethylvinylstannane in 10 mL of DMF was added 0.0052 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 24 h at room temperature. The reaction mixture was quenched with water, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on silica eluting with 10:1 hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.217 g (58%) of the desired product as a yellow oil: IR (Nujol) ν 2004.6 (vs), 1911.8 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.14–6.23 (m, 1 H), 5.40–5.42 (t, 2 H, J = 2.3 Hz), 5.23, 5.37 (dd, 1 H, J = 0.20 Hz), 5.27–5.28 (t, 2 H, J = 2.3 Hz), 5.20, 5.32 (dd, 1 H, J = 0.32 Hz), 0.358 (s, 3 H, J_{W-H} = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ 229.01, 216.09, 128.00, 116.25, 109.68, 89.12, -29.37. Anal. Calcd for $C_{11}H_{10}O_3W$: C, 35.32; H, 2.695. Found: C, 35.41; H, 2.71.

Preparation of Tricarbonyl[[2-(trimethylsilyl)-1(*E*)-ethenyl]-η^5-cyclopentadienyl]methyltungsten.



To a solution of 0.237 g (0.500 mmol) of tricarbonyl(iodo-η^5-cyclopentadienyl)methyltungsten and 0.158 g (0.600 mmol) of [2-(trimethylsilyl)-1(*E*)-ethenyl]trimethylstannane in 10 mL of DMF was added 0.0052 g (2 mol %) of bis(acetonitrile)palladium dichloride under argon. The mixture was stirred for 12 h at room

temperature. The reaction mixture was quenched with water, buffered at pH 8, extracted with ether (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude material was purified by preparative-scale TLC on alumina eluting with 10:1 hexane, extraction of the yellow band with ether, and removal of the solvent under reduced pressure to give 0.126 g (56%) of the desired product as a yellow oil: IR (Nujol) ν 2016.4 (vs), 1927.1 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.32, 6.26 (d, 1 H), 6.04, 5.98 (d, 1 H), 5.41-5.42 (t, 2 H), 5.25-5.27 (t, 2 H), 0.304 (t, 3 H, J_{W-H} = 1.8 Hz), 0.0962 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 229.04, 216.20, 134.14, 133.04, 110.99, 89.03, 88.85, -1.257, -28.61; HRMS exact mass for $C_{14}H_{18}O_3{}^{28}Si^{184}W$, calcd m/z 446.0536, found 446.0529. Anal. Calcd for $C_{14}H_{19}O_3SiW$: C, 37.68; H, 4.292. Found: C, 37.73; H, 4.07.

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Synthesis of 2-Ferrapyridine Complexes and Their Use as Precursors for Substituted Pyridinones and Pyrroles

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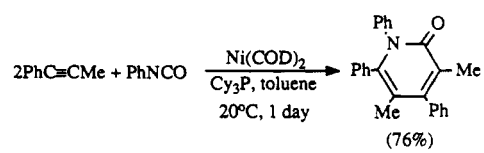
The 2-ferra-3-azetine complexes $Fe_2(\mu\text{-}CHCH{=}NR)(CO)_6$, which form from the reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with phosphinimines, have been found to react photochemically with a variety of alkynes ($R^1C{\equiv}CR^2$) by inserting the alkyne into the four-membered metallacycle to give the 2-ferrapyridine complexes $Fe_2(\mu\text{-}C(R^1)C(R^2)CHCH{=}NR)(CO)_6$. Two of the 2-ferrapyridine complexes have been crystallographically characterized and shown to consist of six-membered metallacycles having adjacent iron and nitrogen atoms with this metallacycle π-coordinated to the second iron atom by three carbon atoms and an Fe-Fe bond. Terminal alkynes (R^1 = Me, Ph, Bu^t, $SiMe_3$) undergo the insertion regioselectively to give only the 2-ferrapyridine isomer with the substituted carbon adjacent to the iron atom. Unsymmetrical internal alkynes insert to give generally a mixture of isomers which is influenced by the steric and electronic nature of the alkyne substituents. The 2-ferrapyridine complex $Fe_2(\mu\text{-}C(Ph)CHCHCH{=}NBu^t)(CO)_6$ was shown to undergo a ring contraction when heated at 160 °C under CO (500 psi) to give the new 2-ferra-3-azetine complex $Fe_2\{\mu\text{-}C[CH{=}C(Ph)(H)]CH{=}NR\}(CO)_6$, which has also been crystallographically characterized and has a vinyl substituent attached to the 3-carbon of the 2-ferra-3-azetine ring. When heated, the 2-ferrapyridine complexes released 2-pyridinones and pyrroles with the ratio of these products dependent upon the ring substituents and the conditions employed. For example, the 2-ferrapyridine complexes prepared from terminal alkynes gave 2-pyridinones as the major products. The reaction of 2-ferrapyridine complexes prepared from internal alkynes gave mixtures of 2-pyridinones and pyrroles. The presence of electron-donating substituents on the 2-ferrapyridine ring favored the formation of 2-pyridinones, as did the presence of halide ion and an atmosphere of CO in the thermolysis reactions.

Introduction

The pyridinone framework is an integral part of many biologically active molecules.[1,2] As a consequence, there has been a great deal of interest in the development of new synthetic procedures for this class of heterocycles.[1] There are many synthetic routes to substituted pyridinones which involve classical organic reactions,[1,2] but only a few organometallic methods for the preparation of these compounds have been described.[3] The latter routes generally involve the metal-assisted regiospecific coupling of an isocyanate unit with 2 equiv of an alkyne to yield either tri- or pentasubstituted 2-pyridinones. For example, Hoberg showed that unsymmetrical alkynes react with isocyanates in the presence of a nickel catalyst to produce 2-pyridinones with the larger substituent in the 4- and 6-positions as illustrated in eq 1.[3b] In a complementary



(76%) (1)

route, Hong and Diversi used a cobalt catalyst to produce trisubstituted 2-pyridinones from terminal alkynes and

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