Nuclear Magnetic Resonance Studies of Alkynes as Four-Electron Donor Ligands in Monomeric Tungsten(II) Complexes

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Abstract: Tungsten alkyne complexes of the type $W(CO)(R^1C\equiv CR^2)(S_2CNR_2)_2$ have been prepared for $R^1 = R^2 =$ H, Me, Et, Ph and $R^1 =$ H, $R^2 =$ Ph by allowing tricarbonylbis(dithiocarbamato)tungsten(II) to react with the appropriate alkyne in toluene at ambient temperature. Ethylene does not react with the $W(CO)_3(S_2CNR_2)_2$ reagent under the same conditions. In contrast to the alkynes, phosphorus ligands such as PPh_3, PEt_3, $P(n\text{-}Bu)_3$, and $P(OEt)_3$ displace only one carbon monoxide from the tungsten tricarbonyldithiocarbamate complex to form $W(CO)_2L(S_2CNR_2)_2$ products. Reaction with bis(diphenylphosphino)acetylene initially forms the phosphorus bound dicarbonyl product analogous to the complexes resulting from substitution of one carbon monoxide with a simple phosphorus donor ligand. The orange solid which is isolated undergoes a ligand rearrangement when dissolved in acetone and loses another carbonyl ligand to form the green monocarbonyl derivative $W(CO)(\eta^2\text{-}Ph_2PC\equiv CPPh_2)(S_2CNR_2)_2$ which is analogous to the other alkyne complexes isolated. The symmetrically substituted alkyne ligands undergo a fluxional process which averages the two ends of the bound alkyne at room temperature while the four independent alkyl groups of the two dithiocarbamate ligands remain distinct. Activation energies of 11–12 kcal mol^{-1} characterize the alkyne rotations investigated. The NMR properties of $W(CO)(PhC\equiv CH)(S_2CNR_2)_2$ are consistent with the existence of only one isomer in solution, and the relative orientation of the acetylene substituents in solution has been determined by employing the heteronuclear Overhauser effect by selectively saturating protons while monitoring the ^{13}C NMR of the cis carbon monoxide ligand. Comparison of the NMR data obtained for $PhC\equiv CH$ as a ligand with the NMR properties of $W(CO)(HC\equiv CH)(S_2CNR_2)_2$ leads to the conclusion that the proximal acetylenic proton couples to the carbon-13 of the carbonyl ligand much more effectively than does the distal acetylenic proton. Hybridization of the acetylenic carbons has been probed by measuring $^1J_{C-H} = 210$ Hz. The low-field ^{13}C chemical shifts of acetylenic carbons in these tungsten complexes (in the range of 200–210 ppm below Me_4Si) suggest that the mode of alkyne–metal bonding may be correlated with ^{13}C NMR data. We believe that the chemical reactivity patterns and spectroscopic data reported provide support for the four-electron donor role of alkynes in these monomeric tungsten(II) complexes.

Introduction

The number of mononuclear metal complexes which contain coordinated acetylene[1] remains surprisingly small in view of the extensive coordination chemistry which is known for other alkyne derivatives.[2] A perspective on the paucity of transition metals bound to unsubstituted acetylene can be gained by comparison with the much larger number of metal complexes which are known to contain the weak donor dinitrogen as a ligand.[3] Despite mounting evidence in support of the bonding dichotomy possible for acetylene as a variable electron donor when bound to a single metal center, the notion that alkynes can fulfill a dual role as either two- or four-electron donors in monomeric organometallic complexes has not yet permeated the descriptive chemistry of these unsaturated ligands. We wish to report spectroscopic properties associated with bound alkynes which we believe provides additional data in support of the four-electron donor model for the unsaturated ligand in these complexes of tungsten(II).

A mononuclear tungsten complex containing unsubstituted acetylene, $W(CO)(HC_2H)(detc)_2$ (detc = *N,N*-diethyldithiocarbamate), has been isolated and structurally characterized by Weiss, McDonald, and co-workers.[4] The ^1H NMR data and the single-crystal X-ray structure were discussed in terms of four-electron donation from the acetylene ligand to the metal. The relative orientation of the π-acceptor carbonyl ligand and the coordinated acetylene supports the concept of donation from both filled acetylene π orbitals as described by these authors.[4] The solution ^1H NMR data reported (a single acetylene proton resonance is observed 13.1 ppm *downfield* from Me_4Si) seemed incompatible with a static structure equivalent to the one present in the solid state which established the existence of two distinct acetylenic proton environments. The single proton resonance attributed to bound acetylene prompted us to undertake variable-temperature NMR studies in an attempt to elucidate the dynamic solution behavior of this acetylene complex and to obtain NMR parameters for the static structure in the slow exchange limit. A new preparative route to complexes of the type $W(CO)(R^1C\equiv CR^2)(dtc)_2$ (dtc = *N,N*-dialkyldithiocarbamate) was developed during the course of this work.

Further motivation for this study was provided by alkyne complexes of metals in which there is some doubt about the nature of the alkyne–metal linkage.[5] In view of the uncertainty surrounding the mode of acetylene binding in mononuclear metal complexes of current interest we undertook a thorough NMR investigation of a series of $W(CO)(R^1C\equiv CR^2)(dtc)_2$ compounds. The resultant data allowed us to determine the energy barrier associated with intramolecular acetylene rotation, assess possible spectral implications of the postulated four-electron donation from acetylene, measure coupling constants associated with this three-membered metallacycle, identify proximal and distal acetylene substituents relative to the cis carbon monoxide ligand by means of heteronuclear NOE enhancement measurements, and correlate ^{13}C chemical shift values with the bonding mode of the acetylene.

Experimental Section

Physical Measurements. ^1H NMR (100 MHz), ^{13}C NMR (25.2 MHz), and ^{31}P NMR (40.5 MHz) spectra were recorded on a Varian XL-100 spectrometer. ^1H chemical shifts are reported relative to internal 1% HMDS, ^{13}C shifts relative to internal 1% Me_4Si, and ^{31}P shifts relative to external 85% phosphoric acid. Tris(acetylacetonato)chromium(III) (10 mg) was added to routine ^{13}C NMR samples as a shiftless paramagnetic relaxation agent. Samples for heteronuclear Overhauser effect studies were carefully purified, outgassed, and sealed in vacuo before use. Infrared spectra were recorded on a Beckman IR4250 spectrometer and calibrated with polystyrene.

Materials and Procedures. All manipulations were performed under an atmosphere of prepurified nitrogen using standard Schlenk tech-

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niques. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl; cyclohexane was distilled from calcium hydride and purged with a nitrogen stream before use; all other solvents were purged with a nitrogen stream and used without further purification. Tungsten hexacarbonyl, iodine, carbon monoxide (unlabeled and carbon-13 enriched), sodium dialkyldithiocarbamates, and various acetylenes were obtained from commercial sources and used without further purification. The procedure described by Tate and Augl was used to prepare $W(CO)(EtC{\equiv}CEt)_3$,[6] and $W(CO)_4I_2$ was prepared photochemically by the method of Colton and Rix.[7]

Tricarbonylbis(*N,N*-dialkyldithiocarbamato)tungsten(II), $W(CO)_3(dmtc)_2$ (1a) and $W(CO)_3(detc)_2$ (1b). In a representative reaction, $W(CO)_4I_2$ (4.49 g, 8.16 mmol) and Na(detc) (3.68 g, 16.3 mmol) were combined in a 100-mL round-bottom flask under nitrogen. Addition of THF (20 mL) via syringe was followed by gas evolution and the formation of a red solution. After 1 h the solvent was removed in vacuo. Freshly distilled toluene (20 mL) was added and the resultant red slurry was stirred under a carbon monoxide atmosphere for 5 min (the product reversibly loses carbon monoxide under vacuum). The slurry was then chromatographed on an alumina column using toluene as the eluent to yield a red solution. The volume was reduced to 5 mL prior to adding cyclohexane (20 mL) and, upon cooling at −20 °C overnight, this solution yielded orange-red, moderately air- and moisture-sensitive crystals of **Ib** (3.14 g, 5.57 mmol), 68%: ^1H NMR ($CDCl_3$) δ 1.22 (t, 12 H), 3.64 (q, 8 H); IR (toluene solution) ν_{CO} 2005, 1923, 1905 cm^{-1}.

Isotopic Enrichment of 1b with Carbon-13 Monoxide. A sample of **1b** was dissolved in toluene and heated at 40 °C under a ^{13}C-enriched CO atmosphere for 10 h. Upon recrystallization from toluene/cyclohexane, red-orange crystals approximately 40% ^{13}CO enriched (monitored by IR) were obtained. Successive operations could produce material which was 90% ^{13}CO enriched: IR (toluene solution) ν_{CO} 1999, 1883, 1970, 1920 (sh), 1898, 1880, 1865 (sh) cm^{-1}.

In the following sequence reactions involving $W(CO)_3(detc)_2$ (**1b**) will be described. $W(CO)_3(dmtc)_2$ (**1a**) behaves in a similar manner in the preparation of compounds reported in this article.

(η^2-Acetylene)carbonylbis(*N,N*-diethyldithiocarbamato)tungsten(II), $W(CO)(HC{\equiv}CH)(detc)_2$ (2b). A solution of **1b** (0.39 g, 0.69 mmol) in toluene (20 mL) was stirred vigorously under a gentle stream of acetylene for 1 h. During this time the red color of the **1b** solution slowly gave way to the characteristic green of the acetylene complex. Solvent removal under vacuum left a green solid which was recrystallized from toluene/cyclohexane to produce green crystals of **2b** (0.29 g, 0.54 mmol), 79%. The crystalline solid is moderately air and moisture stable: ^1H NMR ($CDCl_3$) δ 1.10–1.39 (m, 12 H) 3.49–3.82 (m, 8 H), 13.04 (s, 2 H); IR (toluene solution) ν_{CO} 1925 cm^{-1}.

(η^2-Alkyne)carbonylbis(*N,N*-diethyldithiocarbamato)tungsten(II), $W(CO)(R^1C{\equiv}CR^2)(detc)_2$ ($R^1 = R^2 = Me$; $R^1 = R^2 = Et$; $R^1 = R^2 = Ph$; $R^1 = H$, $R^2 = Ph$). The following preparative procedure is general for all the alkyne complexes listed above. The appropriate alkyne was added in excess (3 mL for liquids, 0.50 g for solids), under nitrogen via syringe, to a red-orange solution of **1b** (0.50 g, 0.89 mmol) in toluene (20 mL). After 5 min the solution had turned green with concomitant gas evolution. The solution was stirred for 1 h and then the solution volume was reduced to cause precipitation of a green solid which was recrystallized from toluene/cyclohexane in greater than 80% yield.

(η^2-Bis(diphenylphosphino)acetylene)carbonylbis(*N,N*-diethyldithiocarbamato)tungsten(II), $W(CO)(Ph_2PC{\equiv}CPPh_2)(detc)_2$ (7b). Solid **1b** (0.31 g, 0.55 mmol) and $Ph_2PC{\equiv}CPPh_2$ (0.32 g, 0.81 mmol) were placed in a round-bottom flask under nitrogen. Upon addition of toluene (20 mL) rapid gas evolution occurred and a deep red solution formed. After 1 h, 25 mL of cyclohexane was added, yielding 0.15 g (0.16 mmol) of $W(CO)_2(Ph_2PC{\equiv}CPPh_2)(detc)_2$ (**8b**), 29%: IR (CH_2Cl_2 solution) ν_{CO} 1922, 1833 cm^{-1}. Solid **8b** was then dissolved in acetone (10 mL) under a nitrogen atmosphere to form a red solution. During the next 10 h a quantitative yield of green air- and moisture-stable crystalline **7b** precipitated from solution; IR (CH_2Cl_2 solution) ν_{CO} 1920 cm^{-1}.

Results

Syntheses. The isolation of tricarbonylbis(dithiocarbamato)tungsten(II)[8] as a stable solid has provided a convenient reagent for the preparation of a number of substituted derivatives. The reaction of an orange toluene solution of $W(CO)_3(dtc)_2$ (dtc = $^-S_2CNR_2$ with R = Me (**1a**) or Et (**1b**)) with excess alkyne proceeds smoothly at room temperature as indicated in Scheme I to produce a green solution from which crystalline $W(CO)(R^1C{\equiv}CR^2)(dtc)_2$ complexes can be isolated. This new synthetic route avoids the presence of triphenylphosphine in the reaction solution and the two carbon monoxide ligands which are replaced by the alkyne donor evolve smoothly from the system during the substitution reaction.

Scheme I

$$W(CO)_3(S_2CNR_2)_2 + R^1C{\equiv}CR^2 \xrightarrow[1\ h]{toluene}$$

1

a, R = Me (dmtc)

b, R = Et (detc)

$$W(CO)(R^1C{\equiv}CR^2)(S_2CNR_2)_2 + 2CO(g)$$

2, $R^1 = R^2 = H$ **5**, $R^1 = R^2 = Ph$

3, $R^1 = R^2 = Me$ **6**, $R^1 = H$; $R^2 = Ph$

4, $R^1 = R^2 = Et$ **7**, $R^1 = R^2 = PPh_2$

Scheme II

$$W(CO)_3(detc)_2 + Ph_2PC{\equiv}CPPh_2 \xrightarrow[1\ h]{toluene}$$

1b, orange

$$W(CO)_2(Ph_2PC{\equiv}CPPh_2)(detc)_2 + CO(g)$$

8b, deep orange

$$W(CO)_2(Ph_2PC{\equiv}CPPh_2)(detc)_2 \xrightarrow[10\ h]{acetone}$$

8b, deep orange

$$W(CO)(Ph_2PC{\equiv}CPPh_2)(detc)_2 + CO(g)$$

7b, green

An important reactivity feature of the parent tricarbonyl species **1** is that it undergoes facile substitution of one carbonyl ligand to form $W(CO)_2L(dtc)_2$ complexes for L = PEt_3, $P(n\text{-}Bu)_3$, and $P(OEt)_3$ in the presence of excess ligand L, but this product resists further carbonyl substitution and only the monosubstituted dicarbonyl species has been isolated. The analogous $W(CO)_2(PPh_3)(dtc)_2$ compound is well characterized,[9] but the preparative route involving $W(CO)_3Cl_2(PPh_3)_2$ as a reactant is suitable only for the triphenylphosphine derivative.

The bis(diphenylphosphino)acetylene ligand has three potential donor sites: the alkyne fragment and the two phosphorus atoms. Previous studies have shown that $Ph_2PC{\equiv}CPPh_2$ behaves almost exclusively as a ligand which prefers to bridge between two metals by coordinating through both phosphorus nuclei,[10] although monodentate coordination by a single phosphorus has also been observed.[11] The reaction of **1** with $Ph_2PC{\equiv}CPPh_2$ can be separated into two distinct steps. Spectral data suggest that a monodentate phosphorus bound dicarbonyl product, $W(CO)_2L(dtc)_2$, which is analogous to the other phosphorus donor derivatives, is the initial product of the substitution reaction in toluene solution. Dissolution of the dark orange phosphorus ligated complex $W(CO)_2(Ph_2PC{\equiv}CPPh_2)(dtc)_2$ (**8b**) in acetone is followed by a ligand rearrangement which is accompanied by loss of carbon monoxide as the solution color changes to deep green. Isolation of the crystalline alkyne bound monocarbonyl compound (**7b**) analogous to the other alkyne complexes results as shown in Scheme II. The infrared spectra reproduced in Figure 1 for **7b** and **8b** in the carbonyl stretching region are representative of other $W(CO)(R^1C{\equiv}CR^2)(dtc)_2$ and $W(CO)_2L(dtc)_2$ complexes reported in the Experimental Section.

The isolation of **8b** and **7b** is to our knowledge the first example of such ambidentate behavior by this acetylenic di-

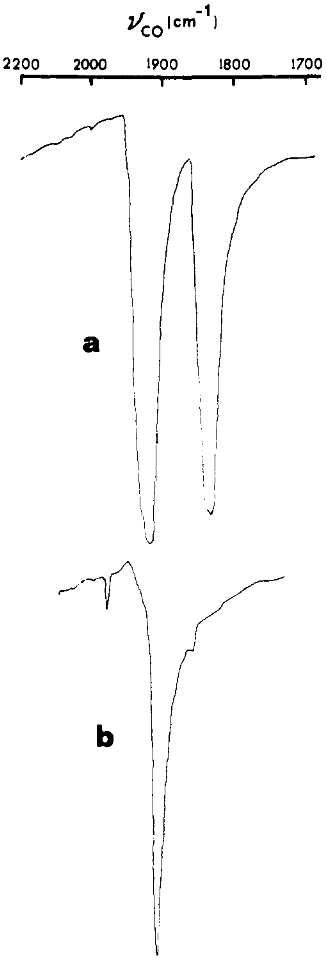


Figure 1. Infrared spectra in the 1700-2200-cm^{-1} region for (a) solid $W(CO)_2(Ph_2PC{\equiv}CPPh_2)(detc)_2$ (**8b**), (b) solid $W(CO)(\eta^2\text{-}Ph_2PC{\equiv}CPPh_2)(detc)_2$ (**7b**). Both spectra were recorded with Nujol mull samples.

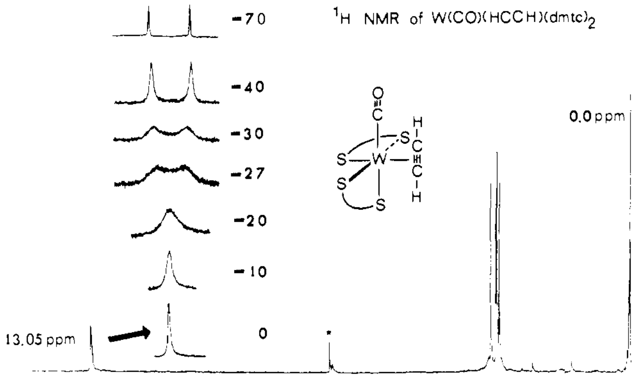


Figure 2. ^1H NMR of $W(CO)(HC{\equiv}CH)(dmtc)_2$ illustrating the temperature dependence of the acetylenic proton resonance (CD_2Cl_2 solvent with HMDS reference; asterisks indicate signals due to toluene, chloroform, and cyclohexane).

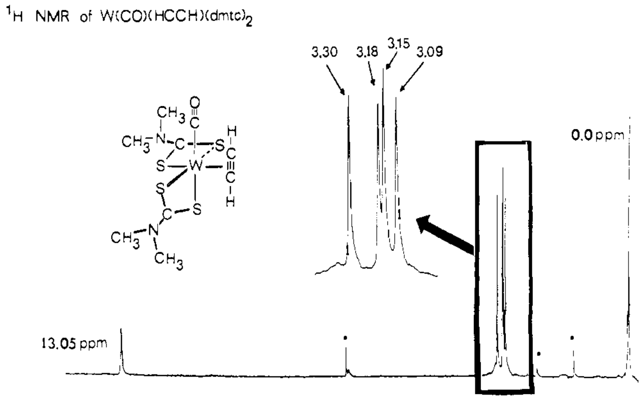


Figure 3. ^1H NMR of $W(CO)(HC{\equiv}CH)(dmtc)_2$ illustrating the four distinct signals associated with the methyl groups of the two *N,N*-dimethyldithiocarbamate ligands.

(tertiary phosphine) where isolation of both compounds has been accomplished. Note that **8b** and **7b** are not isomers since a carbon monoxide ligand is expelled when the metal-alkyne linkage forms.

Nuclear Magnetic Resonance Studies. Variable-temperature NMR studies of **2a** and **2b** indicated that the acetylene ligand is fluxional at ambient temperatures (Figure 2). Two distinct chemical shifts are observed for the two acetylene protons at temperatures below 235 K with a coalescence temperature near 246 K. Similar fluxional behavior is observed for the symmetrically substituted acetylene derivatives **3b** and **7a** (Table I). Variable-temperature ^1H and ^{31}P NMR data for **2a**, **2b**, **3b**, and **7a** were analyzed in the manner reported previously.[8] The rotational activation barrier, $\Delta G^{\ddagger}$, was calculated from the Eyring equation after the Gutowsky-Holm equation was employed to calculate k_{ex} at the coalescence temperature[12] and the fast-exchange and slow-exchange approximations were employed above and below T_c, respectively.[13]

The acetylene rearrangement process is intramolecular as evidenced by retention of coupling information between the acetylene protons and the carbon-13 of the carbon monoxide ligand of **2b** in the fast exchange limit. The two independent values of $^3J_{^1H\text{-}C\text{-}W\text{-}^{13}C}$ observed for the static structure present in the low-temperature limiting spectrum provide quantitative evidence of a substantial difference in the interaction of the two acetylene protons with the cis carbonyl ligand (vide infra).

The alkyl resonances of the dithiocarbamate ligands remain distinct throughout the temperature range investigated.[14a] Interpretation of the methyl group proton signals in **2a** is particularly simple in this regard since four independent singlets are resolved (Figure 3) which must correspond in a 1:1 fashion with the four unique alkyl positions present in the solid-state geometry of **2b**.[4]

Chemical shifts and pertinent coupling constants are listed in ref 14. A ^{13}CO-enriched sample of **2b** displays a carbon-tungsten coupling constant ($^1J_{^{183}W\text{-}^{13}C}$ = 144 Hz; ^{183}W (14.28%), $I = \frac{1}{2}$) which is large relative to the range common for tungsten carbonyl complexes.[15] Three-bond coupling from the acetylene hydrogen through the metal center to carbon-13 of the carbon monoxide ligand is observed in both ^1H and gated decoupled ^{13}C spectra of isotopically enriched **2b**. A triplet is observed for the carbonyl ^{13}C resonance at room temperature ($^3J_{^{13}C\text{-}W\text{-}C\text{-}H}$ = 3 Hz) while in the slow exchange limit at −95 °C the carbonyl resonance is resolved into a doublet with $^3J_{^{13}C\text{-}W\text{-}C\text{-}H}$ = 7 Hz. In conjunction with the average magnitude of 3 Hz observed at ambient temperature, the low-temperature data require that carbon coupling to the two distinct acetylenic hydrogens vary dramatically. The two coupling constants appear to be of opposite sign (±7, ∓1 Hz) in order to quantitatively account for the high-temperature triplet and the low-temperature doublet. The smaller 1-Hz coupling is within experimental error of zero and is not resolved in the low-temperature ^{13}C spectrum, which should formally correspond to a doublet of doublets. The qualitative difference in coupling between the carbonyl ligand and the proximal and distal acetylenic hydrogens is a real phenomenon and independent of the exact numerical value of the smaller coupling constant. The low-temperature ^1H NMR spectrum of a ^{13}CO-enriched sample of **2b** reflects these coupling constant

Table I. Data for Symmetrical Acetylene Complexes

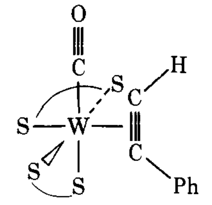
complex	$^1H^a$ or $^{31}P^b$ NMR chemical shift for RC≡CR: ambient temp	low temp (°C)	ΔG‡, kcal mol^{-1}	ν_{CO}, cm^{-1} ^{c}
2a (R = *H*)	13.05^d	12.58, 13.56 (−50)^d	11.9 ± 0.1	1925
2b (R = *H*)	13.04^d	12.53, 13.54 (−70)^e	11.7 ± 0.1	1928
3b (R = CH_3)	3.18^e	3.06, 3.30 (−80)^e	11.1 ± 0.1	1914
7a (R = *P*Ph$_2$)	−14.0	−13.1, −15.0 (−60)	11.4 ± 0.1	1935

^{a} Relative to internal hexamethyldisiloxane, all resonances singlets. ^{b} Relative to external 85% H_3PO_4 at room temperature. ^{c} Toluene solution spectrum. ^{d} $CDCl_3$ solvent. ^{e} CD_2Cl_2 solvent.

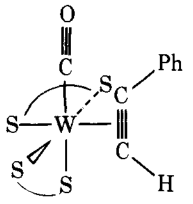
values with the low-field proton (δ 13.56 ppm) exhibiting a broad signal consistent with a 7-Hz doublet superimposed on the singlet present due to molecules containing ^{12}CO and with no resolvable coupling evident in the sharper high-field acetylenic proton resonance (δ 12.58 ppm).

In the absence of literature precedent to guide assignment of the proximal or distal hydrogen as the nucleus more strongly coupled to the carbonyl carbon, we chose to employ the stereochemically rigid phenylacetylene complex as a model system in order to unravel the coupling-constant relationships for the unsubstituted acetylene compound. A successful attempt to measure the coupling of the acetylenic proton of PhC≡CH to the carbonyl ligand in **6b** and to probe the orientation of the unsymmetrical alkyne relative to the cis carbonyl provided a basis for interpreting the structural-spectral relationships in the unsubstituted acetylene complex **2b**.

Assuming that the skeletal geometry of **2b** is appropriate for substituted alkyne complexes implies the possible existence of two isomers for unsymmetrical unsaturated ligands. Spectra of **6b** over the temperature range −60 to +90 °C are compatible with the detection of only a single isomer in solution. Information relevant to the solution geometry of **6b** was obtained by utilizing the heteronuclear Overhauser effect to alter the intensity of the ^{13}C-enriched carbonyl signal by selective irradiation of the acetylene hydrogen. Heteronuclear NOE experiments are known to provide geometrical information regarding the proximity of protons to ^{13}C nuclei.[16] The inverse distance dependence ($1/r^6$), which characterizes the dipole-dipole relaxation mechanism, generally the dominant relaxation process responsible for carbon-13 T_1 values, can be exploited to identify those protons nearest the observed ^{13}C nucleus. A theoretical maximum of 1.99 limits the enhancement factor $f = (I_{NOE} - I_s)/I_s$ for ^{13}C-{^{1}H} experiments. As noted in the Experimental Section sample preparation techniques were employed which excluded oxygen and avoided contamination as completely as possible, but it is also true that contributions to T_1 from any source other than the proton which is saturated can only decrease the enhancement factor, so the presence of paramagnetic species such as adventitious O_2 only serves to lower the observed enhancement and cannot be responsible for any intensity increase.



α



β

The ^{13}C NMR of a 90% ^{13}CO enriched sample of **6b** in benzene-d_6 displayed a 42 ± 2% enhancement in the carbonyl signal upon selective irradiation of the acetylenic hydrogen at δ 13.34 ppm. Only a minor enhancement was observed when the protons of the phenyl ring were saturated (8 ± 3%). These results are presented graphically in Figure 4 and clearly indicate that the hydrogen resides in the proximal or cis position in **6b**, an orientation which places the larger phenyl group in the distal position relative to the carbonyl ligand as in isomer α above.

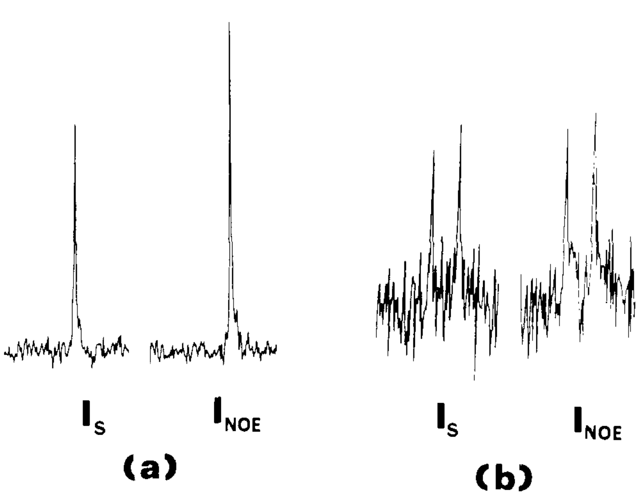


Figure 4. ^{13}C NMR of W(^{13}CO)(HC≡CPh)(detc)$_2$ illustrating the heteronuclear Overhauser effect: (a) enhancement observed upon saturating the acetylenic proton of **6b**; (b) the absence of a significant enhancement observed upon saturating the phenyl protons of **6b**.

Discussion

Chemical Reactivity Patterns. The facile replacement of *two* carbon monoxide two-electron donors during the reaction of W(CO)$_3$(dtc)$_2$ with alkyne derivatives at room temperature contrasts dramatically with the substitution reaction observed with classical two-electron donors, such as phosphines, under the same conditions. A complete lack of reactivity characterizes ethylene as a potential nucleophile in the presence of **1**, and this in itself is strong support for the unique electron-donor capabilities of carbon-carbon triple bond fragments. Furthermore, each phosphine donor provides two electrons and replaces only one carbon monoxide while retaining two carbonyl ligands in order to maintain a total of 18 electrons in the valence shell of the metal.

The reality of four-electron donation from an alkyne ligand to tungsten as reflected in structural[4] and spectroscopic data is substantiated by the lack of chemical reactivity exhibited by W(CO)(RC≡CR)(dtc)$_2$ compounds. These green, crystalline solids are not only thermally stable but also resist decomposition by atmospheric water and oxygen. Such behavior is incompatible with the high reactivity expected for a 16-electron tungsten(II) formulation. The mass of extant data supporting the validity of the effective atomic number rule as applied to low oxidation state group 6 metal compounds containing carbon monoxide ligands suggests that an electron count of 18 provides the best description of these compounds in view of their stability. Several group 6 compounds which have stoichiometries incompatible with the effective atomic number rule if one assumes standard bonding modes for all the ligands (Mo(PMe$_2$Ph)$_4$,[17] Cr(CO)$_2$(dam),[18] [Cr(CO)$_2$(PPh$_3$)]$_2$[19]) are now known to exhibit structures with an unusual coordination mode for one of the ligands which allows the metal to attain an 18-electron configuration.

NMR Properties. Rotation of the acetylene ligand around the bisector of the metal-alkyne isosceles triangle is adequate to account for the observed dynamic NMR properties of the symmetrical alkyne complexes studied. The values of $\Delta G^{\ddagger}$ and ν_{CO} listed in Table I do not reflect a monotonic relationship between the rotational barrier and the carbonyl stretching frequency. The distribution of steric and electronic factors which determine $\Delta G^{\ddagger}$ cannot be extracted from the available data. Given that the total variation in $\Delta G^{\ddagger}$ for the four complexes studied is less than 1.0 kcal mol^{-1}, such an analysis seems inappropriate in any case. The observed decrease in $\Delta G^{\ddagger}$ for the 2-butyne complex as compared to the acetylene case could result from destabilization of the ground state due to steric congestion, but one can also devise rational arguments regarding differences in π bonding as sources of the observed activation energy differences. The similarity of $\Delta G^{\ddagger}$ for R = H, Me, and PPh$_2$ is perhaps surprising in view of the wide variation in steric and electronic factors represented in these three alkyne ligands. Similar fluxional processes involving intramolecular alkyne rotations have been reported by Alt for $(\pi\text{-}C_5H_5)W(CO)(Me)(RC{\equiv}CR)$ complexes.[20] It is noteworthy that the acetylene rotational barriers in the complexes studied by Alt (17-18 kcal mol^{-1}) are significantly larger than those reported here for the dithiocarbamate derivatives (11-12 kcal mol^{-1}).

The rigidity of the dithiocarbamate ligands suggests that a six-coordinate description of the complex in which the alkyne occupies a single site is perhaps preferable to the alternative seven-coordinate model where each acetylenic carbon is considered to occupy a separate coordination position. Although any such preference is merely a formalism, the rationale in the present case is that the dynamic molecular properties of $W(CO)(RC{\equiv}CR)(dtc)_2$ compounds are most easily visualized in terms of an octahedral geometry. Seven-coordinate molecules typically display polytopal rearrangements indicative of only shallow energy minima on the potential surface with no clear preference for one of the idealized geometries. This is exemplified by the rapid averaging of the dithiocarbamate alkyl environments in $W(CO)_3(dmtc)_2$ where a single ^{13}C methyl resonance is observed at ambient temperature with a very low coalescence temperature of −91 °C characterizing the fluxionality of this seven-coordinate compound.[8] An octahedral coordination geometry for tungsten in **2a** is consistent with the observed nonfluxional behavior of the two chelating dithiocarbamate ligands. The intramolecular dynamic process can then be viewed as a simple rotation of the alkyne ligand around the axis passing through the metal and the midpoint of the acetylene triple bond which defines one of the octahedral vertices in this description.

Molybdenum(II) carbonyl dithiocarbamate and dithiophosphinate acetylene complexes which are similar to the tungsten compounds being considered have been reported and both exhibit extreme downfield shifts (δ 12.3 ppm) for the coordinated acetylene protons in accord with NMR behavior considered indicative of four-electron donation.[21] It is interesting that Alt has characterized the related tungsten(II) carbonyl acetylene complex, $(\eta^5\text{-}C_5H_5)W(CO)(HC{\equiv}CH)(CH_3)$,[20] as an electron-deficient 16-electron compound with acetylene contributing only two electrons. According to classical metal-olefin bonding theories an alkyne ligand could donate two electrons in a σ fashion from one filled π orbital while synergistically accepting electron density from the metal into a vacant π^* orbital as in the Dewar-Chatt-Duncanson bonding description applicable to olefins.[22] The ^1H NMR chemical shifts for Alt's tungsten(II) acetylene protons (δ 12.54 and 11.97 ppm for C_2H_2) are in the range found for those systems described as four-electron donor cases above. Group 6 metal-acetylene complexes of the type $(\pi\text{-}C_5H_5)_2M(HC{\equiv}CH)$ which require only two electrons from acetylene to attain the inert gas configuration display ^1H signals between 7 and 8 ppm downfield from Me$_4$Si[23] (cf. free acetylene, δ 2.3).

Table II. Acetylenic Carbon Chemical Shift Values

complex	$\delta(^{13}C)$	ref
2b	206.1, 207.1[b]	this work
6b	205.7[c]	this work
$W(CO)(3\text{-hexyne})_3$[d]	191.1, 170.9	this work
$(\eta^5\text{-}C_5H_5)W(CO)(HC_2H)(CH_3)$	192.5, 187.4	20
trans-$Pt(PMe_2Ph)_2(CH_3)(2\text{-butyne})$	69.5	e
$(Ph_3P)_2Pt(2\text{-butyne})$	112.8	e

[a] Relative to Me$_4$Si. [b] Measured at −50 °C in CDCl$_3$. [c] This is the $\equiv$*C*H ^{13}C chemical shift in CDCl$_3$. [d] This complex was synthesized according to the method described in ref 26. [e] M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Am. Chem. Soc.*, **94,** 5087 (1972).

The unusually low ^1H chemical shifts associated with terminal acetylenic hydrogens in metal complexes where the chemical reactivity of the compound also implicates the alkyne moiety as a four-electron donor provide a convenient spectroscopic probe for assessment of the metal-acetylene bonding mode. In a number of cases the HC≡CH analogues of substituted alkyne metal complexes are not accessible, and the ^{13}C data reported here indicate that a similar role can be ascribed to the carbon-13 chemical shifts of the coordinated carbon nuclei of alkynes. A tabulation of ^{13}C data for coordinated alkynes is presented in Table II.

The data suggest that the ^{13}C chemical shifts for the acetylenic carbons of alkynes filling a role as four-electron donors are significantly below (a difference on the order of 80-140 ppm) those associated with donation of only two electrons from the alkyne to the metal center (see Table II). The role of both bonding π_u orbitals in donating electrons is not in conflict with concomitant acceptance of electron density from the metal into the appropriate vacant π_g^* level of the alkyne analogous to the scheme propose by Chatt[22b] and Dewar[22a] for olefins.

^{13}C NMR provides a sensitive probe of the hybridization at the acetylenic carbon in the form of the ^{13}C-H coupling constant for the bound hydrogen. At room temperature an average $^1J_{^{13}C_\alpha\text{-}H_\alpha}$ value of 210 Hz is observed for the metal-bound acetylene. Assuming that the Fermi contact term is responsible for the coupling allows one to estimate the amount of carbon s character in the C-H bond from the equation[24]

$$\rho_{C\text{-}H} = {}^1J_{^{13}C\text{-}H}(\mathrm{Hz})/500 \qquad (1)$$

A value of ρ = 0.42 results which provides a firm qualitative indication that rehybridization from the free ligand sp hybridization (ρ = 0.50) toward an sp^2 scheme (ρ = 0.33) has occurred. While a quantitative assessment of the hybridization at the acetylenic carbon is not justified, the C-H bond is clearly of intermediate s character relative to the classical sp and sp^2 hybrid orbital descriptions. Weak coupling of the ^{13}C acetylene carbon through the unsaturated linkage to the second acetylene proton is also evident in the ^{13}C NMR spectrum in the fast exchange limit ($^2J_{^{13}C_\alpha\text{-}C_\beta\text{-}H_\beta}$ = 7 Hz).

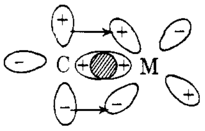
Carbonyl carbon to acetylenic proton coupling results from three-bond coupling through the metal center. The origin of the asymmetry of the coupling between these two cis ligands as reflected in the two $^3J_{^{13}C\text{-}W\text{-}C\text{-}H}$ values remains unexplained. The X-ray structure suggests that the acetylene-tungsten bond is symmetric about the midpoint of the alkyne to a first approximation,[4] and the heteronuclear NOE experiment was required to guide the assignment of the proximal or distal hydrogen as the more strongly coupled nucleus. If one considers the structure in terms of a cis orientation of the carbonyl carbon relative to the proximal hydrogen and correspondingly trans to the distal hydrogen, a three-bond coupling mechanism such as is present between the vicinal hydrogens of olefins would provide an analogy suggesting that the magnitude of the trans coupling would exceed that of the cis.[25] Realistically the presence of a third-row transition metal as one of the bonding links negates the validity of any such simplistic assignment.

Assignment of the low-temperature NMR parameters for **2** can be based on the NMR properties of **6b** and the geometry of **6b** as deduced from the NOE experiment. The $^3J_{^{13}\text{C-W-C-H}}$ of 7 Hz observed for the PhC≡CH hydrogen which is cis to the carbonyl is equal to the coupling constant associated with the downfield acetylene proton of the HC≡CH complex. Hence we assign the downfield signal of the low-temperature ^{1}H NMR spectrum of **2** to the proximal proton. The similarity of the chemical shift of the acetylenic hydrogen for **6b** (13.60 ppm at −60 °C) and the lower field signal of **2b** (13.54 ppm) supports this assignment. This conclusion is also consistent with the qualitative chemical shift expectation resulting from the diamagnetic anisotropy of the CO π bonds influencing the acetylene protons. Since the proximal hydrogen lies in the deshielding cone of the carbonyl ligand it should resonate at a lower field than the distal proton in accord with the conclusion deduced above from the NOE data.

Metal–Alkyne Bonding Considerations. The metal–alkyne bonding in $W(RC{\equiv}CR)_3(CO)$ was accurately described in a publication by King which delineated possible interactions between the two filled π_u orbitals of each acetylene and appropriate metal d orbitals.[26] In essence the application of elementary group theoretical concepts to the pseudotetrahedral geometry of tris(alkyne)carbonyltungsten led to the conclusion that the combination of alkyne π orbitals of A_2 symmetry has no metal orbital counterpart and hence must be rigorously nonbonding. The molecular orbital scheme which results invokes σ donation from each alkyne and the carbon monoxide and also a π-bonding interaction between the tungsten and the perpendicular alkyne orbital combinations transforming as E to total 12 ligand-based electrons in the bonding scheme of the d^6 metal. In the same publication King noted that "bidentate monometallic alkyne ligands appear to be rare outside the series $(\text{alkyne})_3\text{ML}$"; i.e., acetylenes as four-electron donors in monomeric metal complexes were not common even though a total of four electrons were considered to be donated from a single alkyne to two separate metal centers in dimeric complexes such as $Co_2(RC{\equiv}CR)(CO)_6$[27] and $(\pi\text{-}C_5H_5)_2\text{-}Ni_2(RC{\equiv}CR)$.[28]

More recently the metal–acetylene bonding scheme in mononuclear molybdenum complexes has been compared to the π system of the aromatic cyclopropenium cation to account for the extreme downfield shift observed for the acetylenic protons in such compounds.[29] An alternative description rooted in the valence bond formalism has been suggested in which the coordinated acetylene resembles a dicarbene fragment bound to the metal center.[4] Several molecular structures involving substituted acetylenes bound to a group 6 metal center have been reported which provide support for the four-electron donor concept $((\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C{\equiv}CCF_3)(SC_6F_5)$[30a] and $(\eta^5\text{-}C_5H_5)W(O)(PhC{\equiv}CPh)(C_6H_5)$[30b]).

The recent expansion of the chemistry of group 6 alkynes, which are formally electron deficient if one limits alkynes to a one electron pair donor role in these monomeric metal complexes, can be easily rationalized on the basis of the "bidentate monometallic" alkyne–metal bonding interaction described by King and represented schematically below. The π interaction possible between the alkyne and a single metal center is no doubt weaker than the corresponding σ bond owing to geometrical properties which determine the overlap. Nonetheless the stabilization of this perpendicular acetylenic π orbital due to overlap with a metal $d\pi$ orbital fulfills the formal requirements for a two-electron metal–ligand π-bond.



Rationalization of the four-electron donor qualities exhibited by alkynes in these tungsten(II) complexes should surely include the geometric and electronic features at the metal center which promote this interaction. Tungsten(II) is a d^4 ion and hence requires seven classical two-electron donors to attain the inert gas configuration. This concept is substantiated by the large number of seven-coordinate tungsten(II) complexes isolated to date.[31] The general transition-metal preference to form stable six-coordinate complexes and adopt an octahedral geometry is due in part to the well-defined and energetically favorable σ-bond framework which accompanies this particular metal environment. This feature is emphasized by considering the somewhat ill-defined geometries which characterize the adjacent coordination numbers, five and seven. That these odd coordination number geometries are less favorable energetically is suggested by the comparatively small number of examples known relative to the octahedral geometry. Furthermore, several well-established geometries are common for both five and seven coordination, but no single regular geometry is clearly preferable from an energy minimization standpoint. In the case of acetylene complexes described herein, tungsten can adopt an octahedral geometry consistent with the classical metal–ligand σ-bonding scheme. The resultant σ-bond framework generates an antibonding e_g^* d-orbital pair while leaving the t_{2g} $d\pi$ levels available to interact with ligand orbitals of π symmetry. Two orbitals of the $d\pi$ set can overlap with the empty π^* of the cis carbon monoxide ligand. This orbital mixing selectively lowers the energy of these two $d\pi$ orbitals and the four available metal electrons then occupy these stabilized levels. The one remaining $d\pi$ orbital overlaps effectively with the filled acetylene π orbital which is not involved in a dative σ bond to the metal. This metal–alkyne π overlap increases the $d\pi$ energy level while stabilizing the acetylene π level which contains two electrons. The net result is a stable d^4 metal complex best described as an octahedral species.

The implications of variable electron donation from alkyne ligands are of potential importance in organometallic reactions which require facile interplay between 16- and 18-electron complexes. Examples of ligands which can provide either one or three electrons include nitrosyl[32] and allyl.[33] The role of the η^3 to η^1 conversion of the allyl ligand in the hydrogenation of arenes by $(\eta^3\text{-}C_3H_5)Co(P(OMe)_3)_3$[34] suggests that other electronically flexible electron donor ligands may promote catalytic reaction mechanisms. Efforts to explore the chemical reactivity of acetylene complexes in this regard are currently being pursued in this laboratory.

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(14) (a) NMR spectra were recorded in $CDCl_3$ and IR spectra in toluene. σ is reported as parts per million downfield from internal HMDS for ^1H and Me_4Si for ^{13}C except where noted. Complex: ν_{CO} (cm^{-1}); δ (multiplicity, relative intensity) with s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. **2a:** (1928) [^1H] CH_3 3.09 (s, 3 H), 3.15 (s, 3 H), 3.17 (s, 3 H), 3.30 (s, 3 H). **2b:** (1925) [^1H] CH_3 1.10–1.39 (m, 12 H); CH_2 3.49–3.82 (m, 8 H); [^{13}C] (room temperature) CH_3 12.30, 12.43, 12.84; CH_2 44.18, 44.52, 45.99; $\equiv CH$ 206.7; (−50 °C) C_{dtc} 198.9, 211.7; $\equiv CH$ 206.1, 207.3; CO 237.3 **3a:** (1914) [^1H] CH_3 of dmtc and $\equiv CCH_3$ 3.08–3.38 (m). **3b:** (1910) [^1H] (CD_2Cl_2) CH_3 1.00–1.40 (m, 12 H); CH_2 3.4–3.8 (m, 8 H); $\equiv CCH_3$ 3.18 (s, 6 H). **4a:** (1911) [^1H] CH_3(hexyne) 1.22 (t, 6 H); CH_3(dtc) 3.09 (s, 3 H), 3.16 (s, 3 H), 3.17 (s, 3 H), 3.29 (s, 3 H); CH_2(hexyne) 3.76 (q, 4 H). **4b:** (1910) [^1H] CH_3 (hexyne and dtc) 1.04–1.30 (m, 18 H); CH_2 (hexyne and dtc) 3.48–3.88 (m, 12 H). **5a:** (1928) [^1H] CH_3 3.15 (s, 3 H), 3.16 (s, 3 H), 3.20 (s, 3 H), 3.24 (s, 3 H); *Ph* 7.14–7.70 (m, 10 H). **5b:** (1927) [^1H] CH_3 1.07–1.36 (m, 12 H); CH_2 3.44–3.80 (m, 8 H); *Ph* 7.20–7.66 (m, 10 H). **6a:** (1925) [^1H] CH_3 3.10 (s, 3 H), 3.12 (s, 3 H), 3.18 (s, 3 H), 3.24 (s, 3 H); $\equiv CPh$ 7.32–7.93 (m, 5 H); $\equiv CH$ 13.48 (s, 1 H), (−70 °C) 13.66 (s, 1 H). **6b:** (1924) [^1H] CH_3 1.04–1.33 (m, 12 H); CH_2 3.43–3.88 (m, 8 H); $\equiv CPh$ 7.24–7.99 (m, 5 H), $\equiv CH$ 13.34 (s 1 H) (−60 °C) 13.60 (s, 1 H); [^{13}C] CH_3 12.2, 12.4, 12.8; CH_2 43.9, 44.1, 44.5, 45.8; Ph(ortho) 128.5, (meta) 131.8, (para) 129.3, (ipso) 136.4; C(dtc and $\equiv CPh$, unassigned) 199.9, 210.9, 213.1; $\equiv CH$ 205.7; CO 237.9. **7a:** (1937) [^1H] CH_3 2.98 (s 3 H), 3.08 (s, 3 H), 3.13 (s, 3 H) 3.14 (s, 3 H); *Ph* 6.96–7.60 (m, 10 H). **7b:** (1935) [^1H] CH_3 1.12 (q, 12 H); CH_2 3.20–3.68 (m, 8 H); *Ph* 6.80–7.50 (m, 10 H). (b) Pertinent coupling constants for **2b** in hertz at room temperature unless otherwise noted. **2b:** $^1J(W\text{–}C_{CO}) = 144$; $^2J(C_{CO}WC_{C\equiv C}) = 22$; $^3J(C_{CO}WCH) = 3$; (−95 °C) $^3J(C_{CO}WCH_a) = \pm 7$, $^3J(C_{CO}WCH_b) = \mp 1$; $^1J(C_{C\equiv C}H) = 210$; $^2J(C_{C\equiv C}CH) = 7$.

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Resonance Energies of π-Hydrocarbon–Iron Tricarbonyl Complexes[1]

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Abstract: Tricarbonyl(tetrahapto-unsaturated hydrocarbon)iron complexes are described as resonance hybrids of valence-bond structures. Quantitative structure-resonance theory and previously established graph-theoretical algorithms are used to describe the complexes and to calculate resonance energies. The results are in agreement with experimental properties of these complexes.

Resonance energies,[2,3] bond orders,[4,5] heats of formation,[6-8] ionization potentials,[9] and reactivity indexes[10-13] for hydrocarbon π systems can be obtained using an empirical valence bond theory with a highly limited basis of Kekule structures. This theoretical framework is termed structure-resonance theory, and its applications have been recently reviewed.[14] The numerical results correlate precisely with experimental properties and with the results of LCAO-MO-SCF calculations. Graph-theoretical algorithms for counting structures[15,16] and an accurate empirical logarithmic relationship[17] between structure count (SC) and resonance energy (RE) allow the theory to be applied rapidly.

The same formulism can be used to describe transition-metal complexes with π hydrocarbon ligands. This paper summarizes resonance energies for tricarbonyl(tetrahapto-unsaturated hydrocarbon)iron derivatives obtained by this approach. The results allow one to quantitatively rationalize relative stabilities and fluxional behaviors of iron complexes of this type.

Valence Model. A topological, Hückel-type, orbital model is used that has been previously employed by Mingos[18] to discuss the bonding in metal η^3- and η^4-unsaturated hydrocarbon complexes. In this model, the complex is described as a metal–hydrocarbon fragment perturbed to a negligible extent by the carbonyl groups. Justifications derive from experimental studies of photoelectron spectra,[19,20] ab initio calculations,[19,21] semiempirical MO calculations,[22,23] and perturbation theory arguments.[24]

The basic set for tricarbonyl(butadiene)iron and graphs of the bonding network are depicted in **1**. Iron hybrid d_{xz}–p_x and d_{yz}–p_y orbitals are assumed to combine with the organic ligand p orbitals to form a three-dimensional delocalized electronic network containing $n/2$ electrons, where n is the total number

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