Organometallics **1999,** *18,* 3201−3207 3201

Reduction of $[ML(alkyne)_2(\eta\text{-}C_5R'_5)]^+$ (M = Mo or W, L = MeCN or CO, R′ = H or Me, $C_5R'_5 = C_5HPh_4$): Characterization of Radical Intermediates in the Reductive Coupling of Coordinated Alkynes

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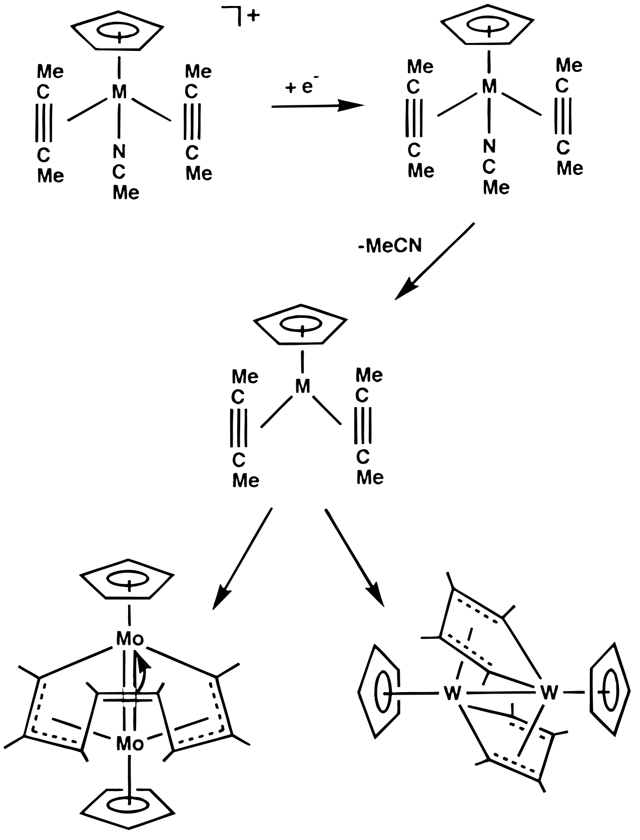
Received February 11, 1999

The complexes $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ (M = Mo or W, R = Me or Ph; R′ = H or Me, $C_5R'_5 = C_5HPh_4$) undergo one-electron reduction to $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]$, which rapidly lose acetonitrile to give the 17-electron complexes $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$. The stability of $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$ depends on R and R′; for R = Ph, the radical is sufficiently stable so that its reduction to the 18-electron anion $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]^-$ is detected in the cyclic voltammogram. Chemical reduction of $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]^+$ with $[Co(\eta\text{-}C_5H_5)_2]$ gives the air-sensitive solid $[Mo(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$, characterized as an alkyne-based radical by ESR spectroscopy, which gives $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]^+$ when treated with $[Fe(\eta\text{-}C_5H_5)_2]^+$ in acetonitrile. The carbonyl cations $[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ (M = Mo, W) undergo two sequential one-electron reductions, the first of which is reversible and gives the 19-electron species $[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]$. The 19-electron radical $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ has been characterized in solution by IR and ESR spectroscopy.

Introduction

The reduction of bis(alkyne) complexes of the type $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ (M = Mo, W) can lead to the isolation of binuclear complexes in which C−C coupling of the alkyne ligands has occurred.[1] For example, treatment of $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ (**1**) with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ or sodium amalgam gives[2] the metallacyclononatetraene complex $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$, with four linked but-2-yne ligands, and $[W(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ reacts with sodium amalgam to give the bis(metallacyclopentadiene) complex $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]$ via pairwise alkyne linking.[3] The postulate[1c,d] of a radical mechanism for the formation of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$ was confirmed in an electrochemical study of **1**.[4] Voltammetry established that the 19-electron complex $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]$, the first product of the reduction of **1**, undergoes very rapid loss of acetonitrile, implying formation of the 17-electron radical $[Mo(MeC_2Me)_2(\eta\text{-}C_5H_5)]$, which couples to form the binuclear product (Scheme 1). Given the unusual C−C coupling reaction of this bis(alkyne) radical (neutral 17-electron organometallic radicals

Scheme 1



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10.1021/om990089l CCC: $18.00

more usually undergo other reactions, i.e., metal−metal bond formation, hydrogen atom loss or gain, etc.[5]), a more systematic study was undertaken of the generation and fate of other species of the type $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$ (M = Mo, W; R = Me, Ph; R′ = H, Me; $C_5R'_5 = C_5HPh_4$). As the present paper shows, the formation of such radicals by reducing $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ is general. Moreover, we demonstrate how the systematic variation of R and R′ leads to the isolation of the radical $[Mo(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$ and provides insight into the possibility of systematic synthesis using the bis(alkyne) radicals $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$.

The effect of the ancillary ligand, L, in $[ML(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ has also been investigated by replacing L = MeCN by L = CO. The π-acceptor CO ligand retards the loss of L from the 19-electron complex $[ML(RC_2R)_2(\eta\text{-}C_5R'_5)]$, thereby affecting the radical reaction pathways. A preliminary study[6] of the reduction of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ suggested that the neutral 19-electron complex $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ was stable on the voltammetric time scale. In this paper we characterize $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ by IR and ESR spectroscopy and demonstrate its slow loss of CO to form the 17-electron radical $[Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$.

Experimental Section

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using dried, distilled, and deoxygenated solvents. Unless stated otherwise, the new complexes are air-stable in the solid state and dissolve in polar solvents such as CH_2Cl_2 and thf to give solutions which only slowly decompose in air. The complexes $[MoMe(CO)_3(\eta\text{-}C_5Me_5)]$, $[MoMe(CO)_3(\eta\text{-}C_5HPh_4)]$,[7] $[WMe(CO)_3(\eta\text{-}C_5Me_5)]$ and $[WMe(CO)_3(\eta\text{-}C_5HPh_4)]$,[8] $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ (**10**),[9] $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ (**2**),[10] and $[Co(\eta\text{-}C_5H_5)_2]$[11] were prepared by published methods. IR spectra were recorded on a Nicolet 5ZDX FT spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL GX270, λ300, or GX400 spectrometers with $SiMe_4$ as internal standard. X-band ESR spectra were recorded on either a Bruker ESP-300E spectrometer or a modified Varian E-4 spectrometer, equipped with variable-temperature accessories and a microwave frequency counter. The field calibration was checked by measuring the resonance of the diphenylpicrylhydrazyl (dpph) radical before each series of spectra. Electrochemical studies were carried out using EG&G model 173 or 273 potentiostats in a traditional three-electrode configuration.[12a,b] The working electrode was Pt; a small disk was used for cyclic voltammetry and a large gauze basket for bulk electrolyses. The reference electrode was either an aqueous saturated calomel electrode (SCE) or a Ag/AgCl wire which was separated from the test solution by a fine-porosity glass frit. Ferrocene was added as an internal standard at an appropriate point in the experiment, and all potentials in this paper are versus that of the ferrocene/ferrocenium couple. Reversible couples are characterized by their $E_{1/2}$ potentials, measured as the average of the cathodic and anodic peak potentials, Ep_c and Ep_a, respectively. Potentials of chemically irreversible systems are given by their peak potentials at a scan rate of 200 mV s^{-1} unless otherwise stated. Solutions were generally 0.5−1.0 mM in the test compound and 0.1 M in the supporting electrolyte $[NBu_4][PF_6]$. IR spectroelectrochemical experiments were accomplished using a thin-layer IR transparent cell.[12c] Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

$[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$ (12). A solution of $[MoMe(CO)_3(\eta\text{-}C_5HPh_4)]$ (1.97 g, 3.49 mmol) in CH_2Cl_2 (50 cm^3) was treated with $HBF_4\cdot OEt_2$ (0.5 cm^3, 3.7 mmol). After 2 h, diphenylacetylene (5.6 g, 31.4 mmol) was added to the purple solution of $[Mo(OEt_2)(CO)_3(\eta\text{-}C_5HPh_4)][BF_4]$ and the mixture heated under reflux for 36 h. The mixture was evaporated to dryness in vacuo and the excess PhC_2Ph removed by treatment with hot toluene (100 cm^3) and then *n*-hexane (30 cm^3). The red-orange residue was then dissolved in CH_2Cl_2; allowing diethyl ether to diffuse slowly into the solution gave orange crystals of the product, 1.83 g (56%).

The complexes $[M(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$ [M = Mo (**11**) or W (**14**)] and $[W(CO)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$ (**15**) were prepared similarly.

$[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$ (6). A mixture of $[W(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$ (**14**) (0.241 g, 0.31 mmol) and Me_3NO (0.023 g, 0.31 mmol) in MeCN (20 cm^3) was heated under reflux until the carbonyl band of the cation was absent from the IR spectrum. The mixture was then evaporated to dryness in vacuo and the residue dissolved in CH_2Cl_2. Allowing diethyl ether to diffuse slowly into the solution gave yellow needles of the product, 0.225 g (92%).

The complexes $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$ (**3**) and $[M(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$ [M = Mo (**4**) or W (**7**)] were prepared similarly.

$[Mo(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$ (8). To a stirred solution of $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$ (4) (85 mg, 0.09 mmol) in CH_2Cl_2 (5 cm^3) at −50 °C was added a solution of $[Co(\eta\text{-}C_5H_5)_2]$ (17 mg, 0.09 mmol) in CH_2Cl_2 (3 cm^3), resulting in a color change from yellow to green. After 10 min the solvent was removed in vacuo to give a green solid, which was dissolved in diethyl ether and filtered through Celite. Concentration of the solution and addition of *n*-pentane at −50 °C gave a fine green precipitate, which was filtered, washed, and dried in vacuo to give a light green, very air-sensitive solid, 20 mg (27%).

Results and Discussion

Synthesis of $[ML(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ (M = Mo or W, L = MeCN or CO, R = H or Me, R′ = H or Me, $C_5R'_5 = C_5HPh_4$). The complexes studied in this work (**1**−**7** and **9**−**15**, Scheme 2) were prepared by published methods[9,10,13] or modifications thereof and characterized by elemental analysis and IR (Table 1) and NMR spectroscopy (Table 2). The ^{13}C NMR spectra are the most informative in showing two resonances for the alkyne carbons, in accord with the structure shown in Scheme 2; the chemical shifts, in the range 150−190

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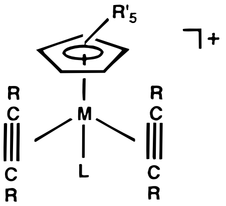
Scheme 2



Complex	M	L	R	R'5	Complex	M	L	R	R'5
(**1**)	Mo	MeCN	Me	H_5	(**9**)	Mo	CO	Me	H_5
(**2**)	Mo	MeCN	Ph	H_5	(**10**)	Mo	CO	Ph	H_5
(**3**)	Mo	MeCN	Ph	Me_5	(**11**)	Mo	CO	Ph	Me_5
(**4**)	Mo	MeCN	Ph	HPh_4	(**12**)	Mo	CO	Ph	HPh_4
(**5**)	W	MeCN	Me	H_5	(**13**)	W	CO	Me	H_5
(**6**)	W	MeCN	Ph	Me_5	(**14**)	W	CO	Ph	Me_5
(**7**)	W	MeCN	Ph	HPh_4	(**15**)	W	CO	Ph	HPh_4

ppm, are consistent with the alkyne ligands acting, formally at least, as three-electron donors.[14]

Electrochemistry of $[ML(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$. The general reductive behavior of the two sets of compounds studied, namely, $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ and $[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$, is described first, followed by the more detailed voltammetry and spectroelectrochemistry of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$.

Reduction of $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$. Each of the 18-electron cations $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ is reduced in an irreversible one-electron process in thf. The initially formed 19-electron species $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]$ (eq 1) undergoes rapid loss of acetonitrile (eq 2), giving rise to the 17-electron species $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$ (Scheme 1). For the diphenylacetylene complexes of molybdenum the 17-electron radical is sufficiently stable so that its one-electron reduction wave is also detected, at a more negative potential than that of the first process, allowing measurement of $E_{1/2}$ for the 17-electron/18-electron couple $[Mo(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]/[Mo(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]^-$ (eq 3). The CV of $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ (**3**) is shown in Figure 1a as an example. The overall electrochemical sequence is therefore an ECE process beginning and ending with 18-electron species:

$$[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+ + e^- \rightleftharpoons [M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)] \quad (1)$$

$$[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)] \rightleftharpoons [M(RC_2R)_2(\eta\text{-}C_5R'_5)] + NCMe \quad (2)$$

$$[Mo(PhC_2Ph)_2(\eta\text{-}C_5R'_5)] + e^- \rightleftharpoons [Mo(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]^- \quad (3)$$

For the MeC_2Me complexes there is little evidence for the 17-electron radicals, as indicated by the virtual absence of a second reduction wave after the initial reduction of, for example, $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ (**1**) (Figure 1b). In this particular case the radical $[Mo(MeC_2Me)_2(\eta\text{-}C_5H_5)]$ couples rapidly to produce[2] the binuclear product in Scheme 1.

Although similar chemical behavior is observed for the tungsten complexes, the voltammetry differs from that of the Mo analogues. The reduction potentials of the 18-electron cations $[W(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ differ significantly from those of the corresponding Mo complexes (Table 3), on average by −0.37 V for a given R and R′ (e.g., compare **5** with **1**, **6** with **3**, and **7** with **4**), whereas those of the neutral 17-electron radicals $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$ do not (average difference = −0.04 V; compare **6** with **3**, and **7** with **4**). The greater negative shift of the reduction wave of the 18-electron tungsten complexes therefore has the effect of decreasing the separation in potentials between the electron-transfer processes in eqs 1 and 3 {compare Figure 1c, which shows the CV of $[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ (**6**), with Figure 1a}. In fact, for $[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]^+$ (**7**) (Figure 1d) the two reduction waves are almost superimposed.

The virtual lack of metal dependence of the reduction potential of the 17-electron radicals $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$ is consistent with the half-filled orbital (SOMO) being based mainly on the alkynes, a conclusion reinforced by ESR spectroscopic measurements (see below). Although the redox orbital (LUMO) of the 18-electron complexes $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ is more highly metal-based, it must also contain considerable alkyne character since the potential shift when the coordinated alkyne is changed from MeC_2Me to PhC_2Ph is 0.43 V (Table 3, e.g., compare Ep_c of **1** with that of **2**). By contrast the potential shift when the cyclopentadienyl ring substituents are changed is small (e.g., compare **2**, **3**, and **4**).

The reduction of complex **2** in MeCN was investigated in order to see if ligand loss (eq 2) is inhibited in the presence of a large excess of the nitrile. Although some chemical reversibility was observed, nitrile loss from the 19-electron complex $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5H_5)]$ was not completely eliminated at a CV scan rate of 0.2 V s^{-1}.

To confirm that reduction of the 18-electron cations $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ gives the corresponding neutral 17-electron radicals $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$ (eqs 1 and 2), the Mo complexes **3** and **4** were treated with the one-electron reductant $[Co(\eta\text{-}C_5H_5)_2]$ in thf ($E_{1/2} = -1.31$ V)[15] and the resulting solutions investigated by ESR spectroscopy. In the case of **4**, the 17-electron radical $[Mo(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$ (**8**) was also generated by adding solid $[Co(\eta\text{-}C_5H_5)_2]$ to a frozen solution of **4** in thf/CH_2Cl_2 (2:1) and allowing the mixture to warm in the cavity of the ESR spectrometer until the spectrum was observed.

In all cases, intense spectra were observed, both in fluid and frozen solutions (Table 4). A rhombic g-tensor assigned to $[Mo(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]$ is apparent from low-temperature spectra; Figure 2 shows that of $[Mo(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$ (**8**) in thf/CH_2Cl_2 (2:1) at 120 K. Considering that the radicals contain a second-row transition metal, the g-values are quite close to that of the free spin. For example, for $[Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ $g_1 = 2.048$, $g_2 = 2.024$, $g_3 = 2.006$ (Table 4); the average of the three anisotropic g-values (2.026) agrees well with the isotropic value of 2.027. The g-values, the lack of observable metal hyperfine splitting in the fluid solution

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Table 1. Analytical and IR Spectroscopic Data for Alkyne Complexes

	complex	color	yield (%)	analysis (%)[a] C	H	N	IR[b]/cm^{-1} ν(CO)
2	$[\mathrm{Mo(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$	orange	70	65.0 (65.1)	4.5 (4.4)	2.2 (2.2)	
3	$[\mathrm{Mo(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$	yellow	71	67.2 (67.1)	5.3 (5.4)	2.1 (2.0)	
4	$[\mathrm{Mo(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})][\mathrm{BF_4}]$	copper	99	75.0 (74.6)	4.7 (4.7)	1.5 (1.5)	
6	$[\mathrm{W(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$	yellow	92	59.6 (59.8)	4.9 (4.8)	1.5 (1.8)	
7	$[\mathrm{W(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})][\mathrm{BF_4}]$	yellow	71	67.6 (68.3)	4.3 (4.3)	1.5 (1.4)	
10	$[\mathrm{Mo(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$	orange	63	64.5 (64.6)	4.0 (4.0)		2074
11	$[\mathrm{Mo(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$	yellow	73	66.6 (66.7)	5.1 (5.0)		2060
12	$[\mathrm{Mo(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})][\mathrm{BF_4}]$	orange	84	73.7 (74.4)	4.4 (4.4)		2058
14	$[\mathrm{W(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$	yellow	37	59.4 (59.3)	4.5 (4.5)		2067
15	$[\mathrm{W(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})][\mathrm{BF_4}]$	yellow	64	68.1 (68.0)	4.3 (4.0)		2063

[a] Calculated values in parentheses. [b] In $\mathrm{CH_2Cl_2}$.

Table 2. ^{1}H and ^{13}C NMR Spectroscopic Data for Alkyne Complexes in $\mathrm{CD_2Cl_2}$

compound	^{1}H	^{13}C
$[\mathrm{Mo(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$, **2**	2.44 (3H, s, *Me*CN), 6.03 (5H, s, $\mathrm{C_5}\mathit{H}_5$), 7.30−7.56 (20H, m, Ph)[a]	4.97 (*Me*CN), 102.36 ($\mathit{C}_5\mathrm{H_5}$), 127.56, 128.54, 128.63, 129.67, 130.56, 133.60, 135.85, 139.55, ($\mathit{C}_6\mathrm{H_5}$), 168.95, 180.43 ($\mathit{C}{\equiv}\mathit{C}$)[a]
$[\mathrm{Mo(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **3**	1.90 (15H, s, $\mathrm{C_5}\mathit{Me}_5$), 2.28 (3H, s, *Me*CN), 7.09−7.47 (20H, m, Ph)[a]	4.80 (*Me*CN), 10.98 ($\mathrm{C_5}\mathit{Me}_5$), 112.56 ($\mathit{C}_5\mathrm{Me_5}$), 126.71, 128.15, 128.21, 128.68, 130.06, 130.79, 134.08, 134.48, 147.68, (*C*6H5), 170.50, 184.72 ($\mathit{C}{\equiv}\mathit{C}$)[a]
$[\mathrm{Mo(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})][\mathrm{BF_4}]$, **4**	2.31 (3H, s, *Me*CN), 6.89−7.60 (41H, m, Ph and $\mathrm{C_5}\mathit{H}\mathrm{Ph_4}$)	5.29 (*Me*CN), 88.97, 117.55 ($\mathit{C}_5\mathrm{HPh_4}$), 127.50, 127.56, 128.44, 128.63, 129.29, 129.60, 129.77, 130.18, 130.23, 130.60, 130.74, 130.85, 131.81, 135.02, 140.11 ($\mathit{C}_6\mathrm{H_5}$) 173.71, 187.34 ($\mathit{C}{\equiv}\mathit{C}$)
$[\mathrm{W(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **6**	2.01 (15H, s, $\mathrm{C_5}\mathit{Me}_5$), 2.44 (3H, s, *Me*CN), 6.99−7.50 (20H, m, Ph)	4.91 (*Me*CN), 11.43 ($\mathrm{C_5}\mathit{Me}_5$), 112.92 ($\mathit{C}_5\mathrm{Me_5}$), 127.23, 128.16, 128.37, 128.83, 128.94, 129.38, 129.87, 130.59, 131.34, 136.71, 136.95 ($\mathit{C}_6\mathrm{H_5}$), 174.31, 186.29 ($\mathit{C}{\equiv}\mathit{C}$)
$[\mathrm{W(NCMe)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})][\mathrm{BF_4}]$, **7**	2.44 (3H, s, *Me*CN), 6.98−7.63 (41H, m, Ph and $\mathrm{C_5}\mathit{H}\mathrm{Ph_4}$)	5.43 (*Me*CN), 88.11, 116.99 ($\mathit{C}_5\mathrm{HPh_4}$), 126.67, 127.89, 128.52, 128.72, 128.79, 129.50, 129.59, 129.95, 130.28, 130.37, 130.51, 130.58, 131.99, 136.25, 136.32, 138.52 ($\mathit{C}_6\mathrm{H_5}$), 175.03, 187.77 ($\mathit{C}{\equiv}\mathit{C}$)
$[\mathrm{Mo(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$, **10**	6.18 (5H, s, $\mathrm{C_5}\mathit{H}_5$), 7.36−7.70 (20H, m, Ph)	102.36 ($\mathit{C}_5\mathrm{H_5}$), 128.15, 129.68, 129.81, 130.54, 130.83, 132.30, 133.35, 133.81 ($\mathit{C}_6\mathrm{H_5}$) 154.96, 168.92 ($\mathit{C}{\equiv}\mathit{C}$), 217.32 (*C*O)
$[\mathrm{Mo(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **11**	1.98 (15H, s, $\mathrm{C_5}\mathit{Me}_5$), 7.20−7.64 (20H, m, Ph)[b]	11.47 ($\mathrm{C_5}\mathit{Me}_5$), 114.43 ($\mathit{C}_5\mathrm{Me_5}$), 127.24, 129.59, 129.81, 130.48, 130.93, 131.91, 132.36, 133.99, ($\mathit{C}_6\mathrm{H_5}$), 156.37, 173.19 ($\mathit{C}{\equiv}\mathit{C}$), 222.34 (*C*O)
$[\mathrm{Mo(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})][\mathrm{BF_4}]$, **12**	7.01−7.66 (40H, m, Ph), 8.34 (1H, s, $\mathrm{C_5}\mathit{H}\mathrm{Ph_4}$)	92.96, 116.06 ($\mathit{C}_5\mathrm{HPh_4}$), 127.69, 128.72, 128.88, 129.03, 129.63, 129.95, 130.24, 130.42, 130.90, 131.04, 131.11, 131.31, 131.67, 132.01, 132.32, 133.40 ($\mathit{C}_6\mathrm{H_5}$) 157.69, 174.04 ($\mathit{C}{\equiv}\mathit{C}$), 222.27 (*C*O)
$[\mathrm{W(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **14**	2.11 (15H, s $\mathrm{C_5}\mathit{Me}_5$), 7.11−7.66 (20H, m, Ph)	11.48 ($\mathrm{C_5}\mathit{Me}_5$), 112.78 ($\mathit{C}_5\mathrm{Me_5}$), 127.43, 129.68, 129.87, 130.57, 131.86, 131.97, 132.08, 132.26, 134.62 ($\mathit{C}_6\mathrm{H_5}$), 155.06, 172.61 ($\mathit{C}{\equiv}\mathit{C}$), 210.30 (CO)
$[\mathrm{W(CO)(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})]$[BF4], **15**	7.01−7.66 (40H, m, Ph), 8.51 (1H, s, $\mathrm{C_5}\mathit{H}\mathrm{Ph_4}$)	90.93, 114.52 ($\mathit{C}_5\mathrm{HPh_4}$), 127.73, 127.83, 128.66, 128.87, 129.12, 129.21, 129.79, 130.05, 130.40, 130.64, 131.02, 131.30, 131.53, 132.08, 132.20, 133.98 ($\mathit{C}_6\mathrm{H_5}$) 155.21, 171.31 ($\mathit{C}{\equiv}\mathit{C}$), 210.85 (CO)

[a] At 213 K. [b] See also ref 6.

spectrum, and the relatively small Mo couplings in the frozen solution spectrum (the splittings of ca. 10 and 14 G on the high- and low-field components, respectively, may be compared with the anisotropic parameter of ca. 50 G for Mo[16]) are all consistent with the half-filled orbital being mainly ligand-based, most likely with a large alkyne contribution. (The 19-electron radicals described below show significantly larger metal hyperfine couplings in the isotropic spectra.)

Although the radicals $[\mathrm{M(RC_2R)_2}(\eta\text{-}\mathrm{C_5R'_5})]$ have not been isolated in a sufficiently pure state for characterization by elemental analysis, $[\mathrm{Mo(PhC_2Ph)_2}(\eta\text{-}\mathrm{C_5HPh_4})]$ (**8**) was prepared as a very air-sensitive green solid from the reaction between **4** and $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2]$ in $\mathrm{CH_2Cl_2}$ at −50 °C. The solid showed an ESR spectrum (in toluene) identical to that described above. Moreover, treatment

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(16) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1977**, *30*, 577.

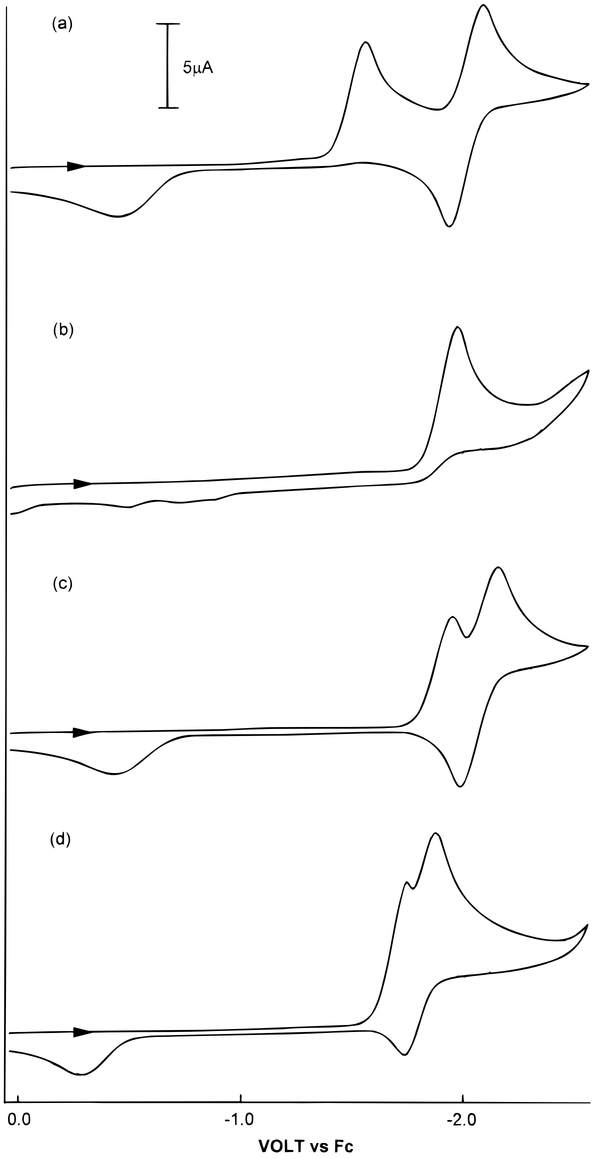

Figure 1. CVs in thf, at a scan rate of 200 mV s^{-1} from 0.0 to −2.6 V of (a) $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$ (**3**), (b) $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ (**1**), (c) $[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$ (**6**), and (d) $[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$ (**7**).

of the green solid in diethyl ether with $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ in acetonitrile gave $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$ in 27% isolated yield (identified by elemental analysis and ^1H NMR spectroscopy), consistent with the presence of unlinked alkynes in complex **8**. Attempts to isolate the tungsten analogue of **8**, namely, $[W(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$, were unsuccessful, although its ESR spectrum was recorded (Table 4) when a frozen solution of $[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]^+$, treated with solid $[Co(\eta\text{-}C_5H_5)_2]$, was allowed to warm in the cavity of the ESR spectrometer.

Table 3. Potentials (V vs Ferrocene) for the Reduction of Alkyne Complexes, in thf/0.1 mol dm^{-3} $[NBu_4][PF_6]$

	complex	$E_{1/2}{}^{a}$	$(Ep)_c{}^{b}$	$E_{1/2}{}^{a,c}$
1	$[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]^{d}$		−1.96	not obsd
2	$[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$		−1.53	−1.84
3	$[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$		−1.56	−2.01
4	$[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$		−1.38	−1.79
5	$[W(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)][PF_6]^{e}$		−2.33	not obsd
6	$[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$		−1.95	−2.07
7	$[W(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$		−1.72	−1.80
9	$[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$	−1.46	-2.32^{f}	
10	$[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$	−1.08	-1.82^{f}	
11	$[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]^{g}$	−1.10	-1.95^{f}	
12	$[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$	−0.93	-1.76^{f}	
13	$[W(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$	−1.78	-2.46^{f}	
14	$[W(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$	−1.28	-2.12^{f}	
15	$[W(CO)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$	−1.22	-1.85^{f}	

[a] Chemically reversible reduction; $E_{1/2}$ calculated from the midpoint of the cathodic and anodic peak potentials. [b] Chemically irreversible reduction; cathodic peak potential given for $\nu = 0.2$ V s^{-1}. [c] Reduction wave for $[M(RC_2R)_2(\eta\text{-}C_5R'_5)]$, the product from the reduction of the corresponding complex $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$. [d] From ref 4. [e] From ref 3. [f] Cathodic peak potential, given for $\nu = 0.2$ V s^{-1}, for the reduction of the 19-electron complex $[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]$. [g] See also ref 6.

Reduction of $[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$. When the MeCN ligand of $[M(NCMe)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ is replaced by a carbonyl group, the 19-electron complex $[ML(RC_2R)_2(\eta\text{-}C_5R'_5)]$ is stabilized in both the thermodynamic sense (the cationic carbonyl complexes are easier to reduce) and in the kinetic sense. Regarding the latter, the one-electron reduction wave of $[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ (eq 4) is either fully or partly chemically reversible at slow CV scan rates and ambient temperatures. Complexes containing but-2-yne give less stable 19-electron complexes than those of diphenylacetylene. In the latter case, the reduction of the 19-electron complex to the (nominal) 20-electron anion (eq 5) can be observed as a second wave with a full cathodic peak height; the CV of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ (**11**) is shown in Figure 3 as an example. Although the second reduction wave is still observed for the but-2-yne complexes, the cathodic peak height is lower owing to the partial decomposition of the 19-electron radical during the time scale of the scan. In general, therefore, the reduction of $[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+$ is an EE process (eqs 4 and 5), with the decomposition reaction of eq 6 affecting the stability of the 19-electron radical when R = Me.

$$[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]^+ + e^- \rightarrow [M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)] \quad (4)$$

$$[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)] + e^- \rightarrow [M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)]^- \quad (5)$$

$$[M(CO)(RC_2R)_2(\eta\text{-}C_5R'_5)] \rightarrow \text{decomposition} \quad (6)$$

Since the decomposition reaction of eq 6 was never too fast to prevent the detection of $[M(CO)(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]$ in CV experiments, the thermodynamically significant quantity $E_{1/2}$ was calculated for each of the carbonyl-containing complexes (Table 3). Thus, for a given R and R′ the carbonyl complexes are easier to reduce than the NCMe analogues, on average by 0.47 V for M = Mo (e.g. **2** vs **10**) or by 0.58 V for M = W (e.g. **6** vs **14**).

As mentioned above, and shown in Figure 3 for **11**, the 19-electron complexes $[M(CO)(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]$ also undergo one-electron reduction, to $[M(CO)(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]^-$, at a potential about 0.7 V more negative than the reduction of $[M(CO)(PhC_2Ph)_2(\eta\text{-}C_5R'_5)]^+$. The reversibility of this wave is a function of the particular complex, the solvent employed, the electrode material,

Table 4. ESR Parameters for Reduction Products[a]

precursor	reductant	product	temp (K)	g_1 [A(M)][b]	g_2	g_3	g_{iso}
3	$[Co(\eta\text{-}C_5H_5)_2]$	$[Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$	77[c]	2.048	2.024	2.006	
			295[c]				2.027
4	$[Co(\eta\text{-}C_5H_5)_2]$	$[Mo(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$	120	2.057	2.028	1.996	
			295				2.026
7	$[Co(\eta\text{-}C_5H_5)_2]$	$[W(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$	120	2.150	2.074	1.970	
			260				2.060
11	$[Co(\eta\text{-}C_5H_5)_2]$	$[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$	77	2.000	1.990	1.983	
			295	[27.1]			1.992
			260[d]	[27.3]			1.991
11	electrolysis[e]	$[Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ (I)[f]	275				2.026
		$[Mo(thf)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ (II)		[23.0]			2.011
		$[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ (III)		[27.5]			1.991
14	$[Co(\eta\text{-}C_5H_5)_2]$	$[W(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$	77	2.024 [37.2]	1.972	1.956	
			295				1.988
15	$[Co(\eta\text{-}C_5H_5)_2]$	$[W(CO)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$	77	2.022 [41.6]	1.986	1.968	
			295				1.980

[a] In CH_2Cl_2/thf (1:2) unless stated otherwise. [b] Metal hyperfine splitting in Gauss from low-field *g*-feature. [c] In thf. [d] In toluene. [e] Cathodic reduction of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)][BF_4]$, at $E_{appl} = -1.5$ V, in thf/0.1 mol dm^{-3} in $[NBu_4][PF_6]$, at 265 K. [f] See text for discussion of assignment.

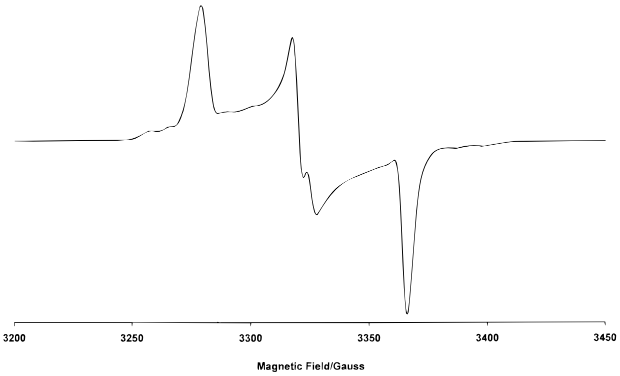

Figure 2. ESR spectrum of $[Mo(PhC_2Ph)_2(\eta\text{-}C_5HPh_4)]$ (**8**) at 120 K in thf/CH_2Cl_2 (2:1).

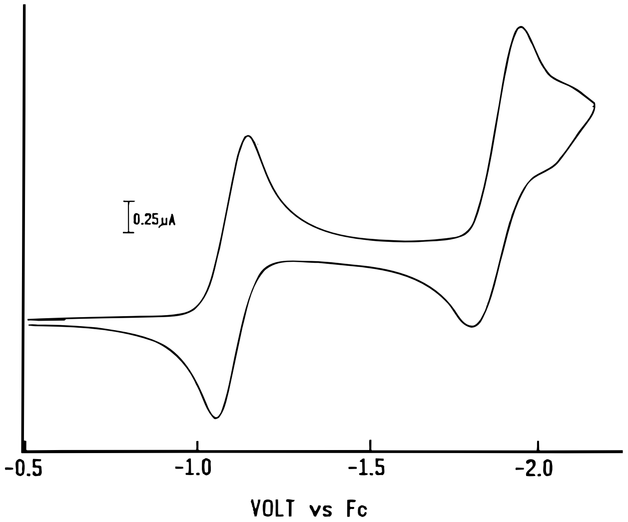

Figure 3. CV of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)][BF_4]$ (**11**) from 0.0 to -2.2 V in thf, at a scan rate of 100 mV s^{-1}.

the temperature, and scan rate. We are engaged in a detailed study of this reduction process. Here, however, we consider the one-electron reduction of a specific complex of this series, namely, $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ (**11**), to detail the electrochemical and spectroscopic properties of one of the 19-electron complexes.

Reduction of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ (11). The reduction of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ (**11**) is diffusion controlled, Nernstian, and fully chemically reversible,[17] in both CH_2Cl_2 and thf down to scan rates, ν, of 0.1 V s^{-1}. Bulk electrolytic reduction in either of these solvents gave coulometric results consistent with the one-electron process of eq 4 (1.0 F/equiv). Although the 19-electron radical $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ decomposed at ambient temperatures in CH_2Cl_2, it is the major product in thf at 265 K. Steady-state voltammograms prior to, and after, electrolysis suggest the yield of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ to be about 60%, with side products present having $E_{1/2} = -1.35$ and -2.06 V; the latter probably corresponds to the reduction of $[Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ (Table 3). On the electrolytic time scale, therefore, the reduction of $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ gives the parent 19-electron radical $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$, lesser quantities of the 17-electron radical $[Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ (formed by loss of CO, eq 7), and a third, unidentified, species.

$$[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)] \rightarrow [Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)] + CO \text{ (slow)} \quad (7)$$

Additional evidence for the suggested products comes from studying the electrolysis solutions by ESR spectroscopy. At 275 K three separate signals, labeled I, II, and III in Figure 4, are observed. Species I is assigned to $[Mo(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$ on the basis that its spectroscopic features ($g_{iso} = 2.026$, no hyperfine splittings) match those of the radical prepared by the reduction of the corresponding acetonitrile complex $[Mo(NCMe)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ (**3**) by $[Co(\eta\text{-}C_5H_5)_2]$ (Table 4). Species III is assigned to the 19-electron complex $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]$; its features ($g_{iso} = 1.991$, $\langle a \rangle Mo = 27.5$ G) match those of the spectrum generated when $[Mo(CO)(PhC_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ **(11)** is treated with $[Co(\eta\text{-}C_5H_5)_2]$ at low temperatures in either toluene or thf (Table 4).

Over the period of about 1 h, resonances I and III disappear from the ESR spectrum of the electrolysis solution and resonance II grows until it is the only signal ($g_{iso} = 2.011$, $\langle a \rangle Mo = 23$ G). The Mo hyperfine splitting in II is close to that observed for $[Mo(CO)(PhC_2$-

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(17) Diagnostics were applied according to the criteria discussed in: Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; Chapter 23.

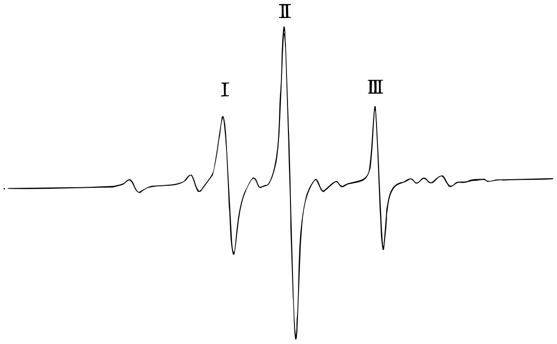

Figure 4. ESR spectra (at 275 K) of solution sampled from cathodic electrolysis ($E_{\rm appl} = -1.5$ V) of 1.2×10^{-3} mol dm^{-3} (**11**) in thf/0.1 mol dm^{-3} [NBu$_4$][PF$_6$], $T = 265$ K. Electrolysis was 95% complete, and coulometry was consistent with the uptake of 1.1 F of charge. Roman numerals refer to the centers of the resonances of the three signals identified in the text.

Ph)$_2$(η-C$_5$Me$_5$)], and on that basis signal II is assigned to another 19-electron complex, most likely the thf complex [Mo(thf)(PhC$_2$Ph)$_2$(η-C$_5$Me$_5$)]. Alkyne loss (or gain) is unlikely given that identical spectra were obtained when the experiment was repeated in the presence of a 20-fold excess of diphenylacetylene.

The 19-electron complex [Mo(CO)(PhC$_2$Ph)$_2$(η-C$_5$Me$_5$)] was also characterized by IR spectroscopy. The cationic precursor [Mo(CO)(PhC$_2$Ph)$_2$(η-C$_5$Me$_5$)]$^+$ (**11**) was electrolyzed in an IR-transparent thin-layer electrochemical cell in thf at 250 K. The carbonyl stretching band (2056 cm^{-1}) gave way to a new band at 1925 cm^{-1} as the electrolysis proceeded (Figure 5), and reoxidation of the product regenerated the original cation in 70% overall yield. A similar experiment in CH$_2$Cl$_2$ at 248 K gave an overall 88% cyclic conversion between [Mo(CO)(PhC$_2$Ph)$_2$(η-C$_5$Me$_5$)]$^+$(**11**)[ν(CO)=2060 cm^{-1}] and [Mo(CO)(PhC$_2$Ph)$_2$(η-C$_5$Me$_5$)] (1919 cm^{-1}).

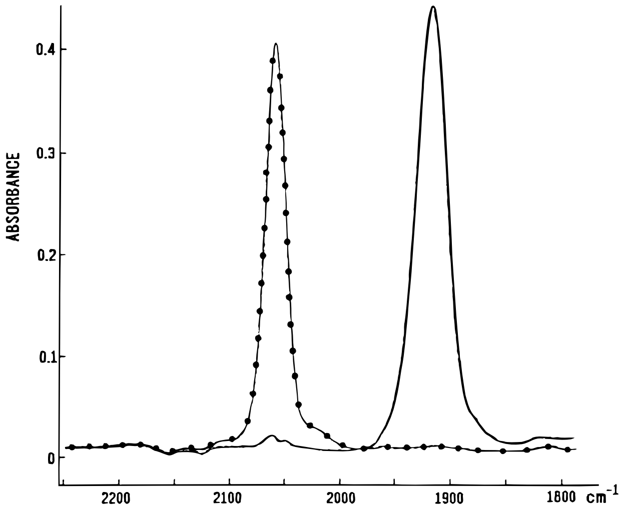

Figure 5. Terminal CO stretching region from IR/spectroelectrochemistry scans of ca. 2.0×10^{-3} mol dm^{-3} (**11**) in CH$_2$Cl$_2$/0.3 mol dm^{-3} [NBu$_4$][PF$_6$], $T = 250$ K. Legend: dots, before electrolysis; solid line, after cathodic electrolysis at $E_{\rm appl} = -1.5$ V resulting in the formation of the 19-electron complex [Mo(CO)(PhC$_2$Ph)$_2$(η-C$_5$Me$_5$)].

Summary

A combined electrochemical and spectroscopic study has shed light not only on the mechanism of the reduction of the bis(alkyne) complexes [ML(alkyne)$_2$(η-C$_5$R′$_5$)]$^+$ (M = Mo or W, L = MeCN or CO, R′ = H or Me, R′$_5$ = C$_5$HPh$_4$) but also on the nature of the reduction products. Thus, the nitrile complexes (L = MeCN) undergo loss of MeCN after one-electron reduction, with the resulting 17-electron, alkyne-based radicals [M(alkyne)$_2$(η-C$_5$R′$_5$)] subsequently reduced to the 18-electron anions [M(alkyne)$_2$(η-C$_5$R′$_5$)]$^-$. By contrast, reduction of the carbonyl analogues (L = CO) gives the metal-based 19-electron radicals [M(CO)(alkyne)$_2$(η-C$_5$R′$_5$)], which are further reduced to [M(CO)(alkyne)$_2$(η-C$_5$R′$_5$)]$^-$. The well-known cationic complexes [ML(alkyne)$_2$(η-C$_5$R′$_5$)]$^+$ are therefore precursors to three other series of potentially useful alkyne-containing reagents, namely, the radicals [M(alkyne)$_2$(η-C$_5$R′$_5$)] and [M(CO)(alkyne)$_2$(η-C$_5$R′$_5$)] and the nucleophilic anions [M(CO)(alkyne)$_2$(η-C$_5$R′$_5$)]$^-$. Future work will explore the chemical reactivity of such reagents.

Acknowledgment. We thank the EPSRC for Postdoctoral Research Associateships (to B.M. and T.J.P.), the National Science Foundation and the Petroleum Research Fund (American Chemical Society) for support at the University of Vermont, and the University of Bristol for a Leverhulme Trust Visiting Fellowship and Benjamin Meaker Visting Professorship (for W.E.G.).

OM990089L