ORGANOMETALLICS

Synthesis, Redox Chemistry, and Electronic Structure of the Alkynyl Cyclopentadienyl Molybdenum Complexes $[Mo(C \equiv CR)(CO)(L_2)Cp']^{n+}$ (n = 0 or 1; R = Ph or C₆H₄-4-Me, L₂ = Ph₂PCH₂CH₂PPh₂ or 2PMe₃, Cp' = Cp or Cp*)

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Supporting Information

ABSTRACT: Two series of bis-phosphine-substituted cyclopentadienyl molybdenum alkynyl complexes, $[Mo(C \equiv CR)(CO)(dppe)Cp']$ and *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$ (R = Ph or C₆H₄-4-Me, dppe = Ph₂PCH₂CH₂PPh₂, Cp' = Cp or Cp*), have been prepared and structurally characterized. One-electron oxidation to the 17-electron radical cations has been investigated by cyclic voltammetry and, for selected Cp* derivatives, by spectroelectrochemical IR and UV–visible methods. Through a combination of experimental measurements (IR and EPR spectroscopy) and DFT-based calculations some important differences between the two series of complexes



 $[Mo(C \equiv CR)(CO)(dppe)Cp']$ and *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$ have been established. In particular, the change in molecular geometry leads to enhanced alkynyl character in the HOMO of $[Mo(C \equiv CR)(CO)(dppe)Cp']$ when compared with the largely metal-centered HOMO of *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$.

INTRODUCTION

The chemistry of carbon chain ligands attached to redoxactive, half-sandwich metal support groups is the focus of intense current research activity. A series of monometallic¹ [M- $(C \equiv C)_n R$] and ligand-bridged bimetallic² $[M - (C \equiv C)_n - M]$ complexes has been investigated, notably for the electron-rich d⁶ metal centers, M = Fe(dppe)Cp^{*},³ Ru(P₂)Cp' (P₂ = 2PPh₃, Cp' = Cp;⁴ P₂ = dppe, Cp' = Cp^{*5}), Re(NO)(PPh₃)Cp^{*},⁶ and Mo(dppe)(η -C₇H₇),⁷ which confer enhanced stability to the products of oxidative redox chemistry. Each of these halfsandwich metal support groups imparts a distinctive character to the redox chemistry of their carbon chain complexes, and this can be attributed, in part, to their electronic structure and the composition of the redox orbital. For example, alkynyl derivatives of $Ru(P_2)Cp'$ and $Re(NO)(PPh_3)Cp^*$ systems feature HOMOs with significant carbon chain contribution derived from good overlap between metal 4d/5d orbitals and the filled π -orbitals of the C \equiv C bond. By contrast, the metal auxiliaries Fe(dppe)Cp^{*} and Mo(dppe)(η -C₇H₇) possess HOMOs which are substantially more metal localized. In the case of Fe(dppe)Cp* this has been rationalized by the reduced overlap of the 3d-orbitals of a first-row metal with the carbon chain ligand π -system. However the metal-centered character of the HOMO of the cycloheptatrienyl-molybdenum complex $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]$ arises from a fundamental difference in electronic structure to

that of related complexes of the Fe, Ru, and Re systems. Thus the increase in ring size from Cp to C₇H₇ promotes strong metal—ring δ -interactions, leading to a reordering of the metal d-orbital manifold and a HOMO with substantial metal d_{z²} character. This in turn results in a reduced interaction between the metal and the alkynyl π -orbitals.^{7a}

These observations suggested that an understanding of the correlation between electronic structure and the redox chemistry of carbon chain complexes could be applied to the fine-tuning of key properties of half-sandwich alkynyl complexes, including reactivity at the carbon chain and spin density distribution, via alteration of variables such as ring size, d-transition series, and the molecular geometry at the metal center. To explore this concept further, we have initiated a series of investigations into the electronic structure and redox chemistry of an extended set of electron-rich, half-sandwich, metal alkynyl complexes.⁸ This report describes the synthesis, redox chemistry, and electronic structures of the cyclopentadienyl molybdenum alkynyl complexes $[Mo(C \equiv CR)(CO)(L_2)Cp']$ (R = Ph, C₆H₄-4-Me; L₂ = dppe or $2PMe_3$, Cp' = Cp or Cp^*). These complexes provide the opportunity to assess the effect of molecular geometry with the "four-leg piano stool" configuration, representing a departure

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Table 1. Compound	Numbering Scheme for
$[MoX(CO)(L_2)Cp']$	and $[Mo(C \equiv CR)(CO)(L_2)Cp']$

complex	X/C≡CR	L ₂	Cp'
1a	Cl	dppe	Ср
1b	Cl	dppe	Cp*
2a	Br	dppe	Ср
3a	Cl	2PPh ₃	Ср
4b	Cl	2PMe ₃	Cp*
5a	C≡CPh	dppe	Ср
5b	C≡CPh	dppe	Cp*
6a	C≡CC ₆ H ₄ -4-Me	dppe	Ср
6b	C≡CC ₆ H ₄ -4-Me	dppe	Cp*
7a	C≡CPh	$(CO)(PMe_3)$	Ср
7b	C≡CPh	$(CO)(PMe_3)$	Cp^*
8a	C≡CPh	2PMe ₃	Ср
8b	C≡CPh	2PMe ₃	Cp^*
9b	$C \equiv CC_6H_4$ -4-Me	2PMe ₃	Cp*

from previous studies. Moreover the location of the alkynyl ligand *trans* to a P-donor or CO ligand in $[Mo(C \equiv CR)(CO)(dppe)Cp']$ and *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$, respectively, presents a further possibility for the control of electronic structure and redox properties by variation of coordination geometry. Finally the combination of CO and C \equiv CR ligands in these complexes provides a dual IR spectroscopic probe for monitoring changes in electron density at the metal and alkynyl ligand resulting from variation in redox state.

RESULTS AND DISCUSSION

Synthetic Studies. A series of precursor halide derivatives $[MoX(CO)(L_2)Cp']$ and the alkynyl complexes $[Mo(C \equiv CR)(CO)(L_2)Cp']$ were synthesized starting from $[MoX(CO)_3Cp']$; a summary of the systems investigated is presented in Table 1.

Each of the halide complexes (1a, 1b, 2a, 3a, 4b) was obtained by direct reaction of $[MoX(CO)_3Cp']$ with the selected phosphine ligand in refluxing toluene and purified by column chromatography on alumina to give the products as orange or yellow solids in moderate yield. All are known complexes,⁹ but a direct thermal substitution method has not been previously employed for the Cp* derivatives 1b and 4b. Replacement of Cp by Cp* (complexes 1b and 4b) resulted in increased reaction times, but the syntheses still proceeded cleanly; in fact, the additional stability conferred by the Cp* ligand is advantageous to the synthesis of 4b since attempts to obtain trans-[MoCl- $(CO)(PMe_3)_2Cp$ by direct reaction of $[MoCl(CO)_3Cp]$ with PMe₃ led to partial decomposition. Selected characterization details (microanalysis, IR, mass, ¹H and ³¹P NMR spectroscopy), sufficient to establish the identity and purity of the materials obtained by the direct carbonyl substitution route, are given in the Experimental Section. The different molecular geometry of the two series of complexes, the *cis*-phosphine, dppe complexes 1a, 1b, and 2a, and the *trans*-phosphine, PPh₃ and PMe₃ systems 3a and 4b, is evident from the number of phosphorus environments in the ${}^{31}P{}^{1}H$ NMR spectra (see Experimental Section).

The successful synthetic routes to the bis-phosphine-substituted alkynyl complexes, as dppe derivatives, **5a**, **5b**, **6a**, and **6b**, and *trans*-PMe₃ complexes **8a**, **8b**, and **9b** are summarized in Scheme 1. Isomerization of a terminal alkyne to a coordinated vinylidene followed by deprotonation is a well-established Scheme 1. Synthetic Routes to $[Mo(C \equiv CR)(CO)(L_2)Cp]$ Complexes^{*a*}



^a Reagents and conditions (i) (a) HC≡CR/MeOH reflux, (b) CO gas;
(ii) NaOMe or KOBu^t in MeOH; (iii) PMe₃, Me₃NO in CH₃CN (1−2 h.); (iv) PMe₃ in toluene, UV (3 h).

protocol for the synthesis of alkynyl complexes at a d⁶ metal center such as Ru(PPh₃)₂Cp or Mo(dppe) $(\eta$ -C₇H₇).^{4,7a} In the current investigation, the $Mo(CO)(L_2)Cp'$ unit is formally Mo(II), d⁴, and, as well-documented, the lower d-electron count leads to a reduced preference for the intermediate vinylidene complex $[Mo(C=CHR)(CO)(L_2)Cp']^+$ versus the decarbonylated four-electron alkyne product [Mo(HC≡CR)(L₂)Cp']⁺.^{14,15} However, as reported previously by Lin et al.,16 reaction of [MoCl-(CO)(dppe)Cp], 1a, with HC≡CPh in refluxing MeOH, followed by sequential treatment with CO and NaOMe, can afford [Mo- $(C \equiv CPh)(CO)(dppe)Cp]$, 5a, via the intermediate η^2 -alkyne and η^{1} - vinylidene complexes [Mo(HC=CPh)(dppe)Cp]Cl and [Mo-(C=CHPh)(CO)(dppe)Cp]Cl. This method was extended to the preparation of the new derivatives $[Mo(C \equiv CC_6H_4-4-Me)(CO)-$ (dppe)Cp], 6a, and the pentamethylcyclopentadienyl analogues $[Mo(C \equiv CR)(CO)(dppe)Cp^*] (R = Ph, 5b, R = C_6H_4-4-Me,$ 6b), demonstrating flexibility of the synthetic route in terms of alkynyl substituent and substitution at the cyclopentadienyl ring. The intermediate Cp^* vinylidene complexes [Mo(C=CHR)(CO)(dppe)Cp*]⁺ exhibited enhanced stability with respect to loss of CO, but the syntheses of the Cp* alkynyls 5b and 6b were still best conducted including CO as a reagent.

Attempts to effect an analogous synthesis of *trans*-phosphine alkynyl complexes commencing from *trans*-[MoCl(CO)(PPh₃)₂-Cp], **3a**, or *trans*-[MoCl(CO)(PMe₃)₂Cp^{*}], **4b**, were unsuccessful; however an alternative route starting from [Mo(C=CR)-(CO)₃Cp'] (R = Ph or C₆H₄-4-Me) involving stepwise substitution of CO by PMe₃ was productive. In the first step, Me₃NO-assisted decarbonylation of [Mo(C=CR)(CO)₃Cp'] in NCMe¹⁷ in the presence of PMe₃ afforded the monosubstituted derivatives [Mo(C=CR)(CO)₂(PMe₃)Cp'] (isolated and fully characterized for the examples R = Ph, Cp' = Cp, **7a**; Cp' = Cp*, **7b**). Subsequent photolysis of [Mo(C=CR)(CO)₂(PMe₃)Cp'] with excess PMe₃ in toluene resulted in partial conversion to

Table 2.	$^{13}C{^{1}H}$	} NMR Data fo	r [Mo(C≡C	$(CO)(L_2)Cp']^a$	
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	Cα	C_{β}	СО	Cp' (Cp or Cp^*)	L/L_2 = dppe or PMe ₃	R
5a	119.8, d, br, J(P-C) са. 47	123.6	245.2, d, J(P—C) 22.1	91.1	141.8–127.2, PPh ₂ ; 31.8, m, CH ₂ ; 28.6, m, CH ₂	b
5b	135.2, d, br, J(P–C) ca. 53	123.1	246.1, d, J(P-C) 19.1	101.5, 10.7	138.5–127.5, PPh ₂ ; 31.0, m, CH ₂ ; 27.0, m, CH ₂	Ь
6a	117.1, dd, J(P—C), 49, 3.9	126.1	245.2, d, J(P–C) 22.1	91.0	141.9-127.6, PPh ₂ ; 31.7, m, CH ₂ ; 28.7, m, CH ₂	21.8, C_6H_4 -Me-4 ^b
6b	not observed	121.6	245.9, d, J(P-C) 20.1	101.4, 10.7	138.7–126.9, PPh ₂ ; 31.1, m, CH ₂ ; 27.0, m, CH ₂	21.1, C ₆ H ₄ Me-4 ^b
7a	109.6, d, <i>J</i> (P–C) 48.3	126.9	252.9, d, <i>J</i> (P–C) 31.2; 238.1, br	91.8	19.7, d, <i>J</i> (P–C) 33.2	130.3, d, <i>J</i> (P–C) 3, C _{o/m} ; 128.0, C _{i/o/m} ; 125.1, C _p
7b	120.8, d, <i>J</i> (P–C) 7.3	126.3, br	256.4, d, J(P–C) 0.2; 241.5, br	104.2, 11.2	18.0, d, <i>J</i> (P–C) 30.2	130.1, d, J(P–C) 2, C _{o/m} ; 128.8, d, J(P–C) 3, C _i ; 128.0, s, C _{o/m} ; 124.7, C _p
8a	129.7, t, J(P—C) 47.8	124.5, br	259.0, t, J(P-C) 30.5	88.7	18.8, m	128.6, m, C _{o/m} ; 128.0, br, C _i ; 127.0, C _{o/m} ; 123.0, C _p
8b	137.0, t, J(P-C) 49.2	126.0, br	267.2, t, J(P-C) 33.2	100.6, 10.8	17.7, m	128.4, br, C _i ; 128.3, m, C _{o/m} ; 127.0, C _{o/m} ; 122.7, C _p
9b	134.8, t, <i>J</i> (P–C) 49.8	125.6, br	267.6, t, J(P-C) 33.2	100.6, 10.8	17.7, m	138.5, Cp, 128.9, C _i ; 128.1, 127.8 C _{o/mj} 21.3, C ₆ H ₄ Me-4

^{*a*} 100 MHz spectra; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; chemical shifts downfield from SiMe₄, coupling constants in Hz. In CDCl₃ solution unless stated otherwise. ^{*b*} Assignment of aryl carbons of the alkynyl substituent R impeded by overlap with dppe Ph carbons.

the required bis-substituted complexes *trans*- $[Mo(C \equiv CR)(CO)-(PMe_3)_2Cp']$ (R = Ph, Cp' = Cp, **8a**; Cp' = Cp*, **8b**; R = C₆H₄-4-Me, Cp' = Cp*, **9b**), which were separated from their precursors by chromatography on alumina and isolated as yellow-orange solids. With the exception of $[Mo(C \equiv CPh)(CO)(dppe)Cp]$, **5a**, the alkynyl complexes presented in this work have not been reported previously, although analogues of **7a** and **8a** (notably *trans*- $[Mo(C \equiv CBu^t)(CO)(PMe_2Ph)_2Cp])^{14}$ are known. The phosphine-substituted derivatives of the Cp* system, i.e., **5b**, **6b**, **7b**, **8b**, and **9b**, appear to be the first examples of complexes of this type.

The alkynyl complexes 5a/b, 6a/b, 7a/b, 8a/b, and 9b were characterized by microanalysis, mass spectrometry, infrared spectroscopy, and by ¹H, ³¹P $\{^{1}H\}$, and ¹³C $\{^{1}H\}$ NMR spectroscopy (see Experimental Section and Table 2). Parameters diagnostic of the presence of the alkynyl ligand in these systems are the C_{α} resonance in the ¹³C{¹H} NMR spectrum and the IRactive $\nu(C \equiv C)$ band. In the case of the cyclopentadienyl dppe complexes [Mo(C=CR)(CO)(dppe)Cp] (5a and 6a), δC_{α} is located in the range 117–120 ppm; for 6a, a resolved doublet of doublets pattern [J(P–C) \approx 50, 4 Hz] was observed for C_{α}, consistent with coupling to two inequivalent phosphorus environments. In the Cp* derivative [Mo(C≡CPh)(CO)(dppe) Cp^*], **5b**, C_{α} is shifted to low field by comparison with **5a** and is observed at δ 135.2 as a broad doublet with $J(P-C_{\alpha}) \approx 53$ Hz. For $[Mo(C \equiv CC_6H_4-4-Me)(CO)(dppe)Cp^*]$, **6b**, a shift in C_{α} to high field by ca. 2 ppm is expected, resulting from the more strongly donating alkynyl substituent, and attempts to locate C_{α} were unsuccessful, probably as a consequence of overlap of the C_{α} resonance with the $C_{o/m}$ carbons of the dppe Ph groups. A doublet resonance was also observed for C_{α} in the monophosphine complexes $[Mo(C \equiv CPh)(CO)_2(PMe_3)Cp']$, 7a/b, and the detection of two discrete resonances for the carbonyl carbons establishes a cis-carbonyl geometry.^{17,18} In the trans bis-phosphine complexes *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$, 8a/b and 9b, C_a is observed as a triplet around 130-135 ppm with a J(P-C) coupling of ca. 50 Hz to the two equivalent phosphorus atoms.

The ν (C=C) band in the IR spectra of the dppe derivatives 5a/band 6a/b lies in a narrow range around 2070 cm⁻¹, toward the high end of values observed for $[M(C \equiv CR)(dppe)(\eta-L)]$ (R = Ph, C_6H_4 -4-Me; M = Fe or Ru, L = Cp, Cp*; M = Mo, L = C_7H_7).^{4,6,7} However, complexes trans- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$ (8a/b and 9b), in which the alkynyl ligand is positioned *trans* to the strongly π -accepting CO ligand, exhibit $\nu(C \equiv C)$ approximately 20 cm⁻ lower than the analogous dppe systems where the alkynyl ligand is arranged trans to a P-donor atom. An additional IR spectroscopic handle in complexes of the type $[Mo(C \equiv CR)(CO)(L_2)Cp']$, not available to related investigations on the systems $[M(C \equiv CR)]$ $(dppe)(\eta-L)$] (M = Fe or Ru, L = Cp, Cp*; M = Mo, L = C₇H₇), is the carbonyl $\nu(CO)$ band. The principal factor governing $\nu(CO)$ is the cis versus trans geometry of the complex with trans-phosphine complexes exhibiting ν (CO) significantly lower (60–70 cm⁻¹) than analogous dppe derivatives. This feature is also evident for halide analogues (cf. [MoCl(CO)(dppe)Cp], 1a, and trans-[MoCl(CO)- $(PPh_3)_2Cp$], 3a; $\nu(CO)$, (CH_2Cl_2) : 1a, 1847 cm⁻¹; 3a, 1792 cm⁻¹) and probably reflects the strong π -donor capacity of both halide and alkynyl ligands positioned trans to the carbonyl. In fact for any two related complexes $[MoX'(CO)(L_2)Cp']$ (X' = Cl or C=CR), the change in ν (CO) on substitution of Cl by C=CR is not more than a few wavenumbers. This π -donor halide to π -acceptor carbonyl interaction may strengthen the Mo-Cl bond in complexes 3a and 4b and account for their lack of reactivity toward terminal alkynes. Finally, $\nu(CO)$ is sensitive to substitution of Cp by Cp^{*} with a shift of approximately 20 cm⁻¹ to lower wavenumber in all Cp* derivatives.

Structural Investigations. The X-ray crystal structures of the bis-phosphine alkynyl complexes **5b**, **6a**, **6b**, **8a**, **8b**, and **9b** have been determined, and important bond lengths and angles are summarized in Table 3. Representative structures, **6a**, **6b**, **8a**, and **8b**, are shown in Figures 1 to 4, respectively, together with details of the structure of the monophosphine derivative **7b** (Figure 5).

In the series of complexes **5b**, **6a**/**b**, **8a**/**b**, and **9b**, the Mo $-C_{\alpha}$ bond length lies in the approximate range 2.12–2.14 Å, consistent with typical values for 18-electron molybdenum alkynyl

Table 3. Key Bond Lengths (Å) and Angles (deg) for $[Mo(C_{\alpha} \equiv C_{\beta}R)(CO)(L_2)Cp']$





Figure 1. Plot of the molecular structure of 6a showing the atomlabeling scheme. In this and all subsequent structural figures, thermal ellipsoids are plotted at 50% probability. Hydrogen atoms have been omitted for clarity.

complexes ([Mo(C=CPh)(dppe)(η -C₇H₇)], 2.138(5) Å,^{7a} [MoH₃(C=CBu^t)(dppe)₂], 2.175(10) Å,¹⁹ and [Mo(C=CPrⁿ) (CO)₂(dppe)(NO)], 2.182(4) Å²⁰). The Mo–P distances also lie within normal ranges, although the trend of elongation of Mo–P_{cis} with respect to Mo–P_{trans} observed for [MoX(CO)-(dppe)Cp] (X = Br,³ Cl²¹) is not seen in **5b**, **6a**, or **6b**. The Mo–CO bond length is sensitive to the identity of the Cp ligand, with shorter bond distances normally observed for the more electron rich Cp* complexes.

A key structural feature of four-leg piano stool systems $[ML_4Cp']$ is distortion of the positions of the tetrapodal L ligands out of the pseudosquare plane. These distortions can be quantified by consideration of (i) the angles between mutually *trans* ligands and (ii) the parameter θ^{22} (also designated α^{23}), which defines the Cp°-Mo-(Ligand) angle (Cp° = centroid of the Cp' ring). These data for the alkynyl complexes **5b**, **6a/b**, **8a/b**, and **9b**



Figure 2. Plot of the molecular structure of 6b showing the atomlabeling scheme.

together with the related chloride complexes [MoCl(CO)(dppe)-Cp], 1a,²¹ and *trans*- $[MoCl(CO)(PMe_2Ph)_2Cp^*]$, 4b',²⁴ are summarized in Table 4.

Inspection of Table 4 reveals that there is a much greater disparity in the magnitudes of the *trans* angles in the dppe complexes **Sb** and **6a/b** than for the PMe₃ complexes **8a/b** and **9b**. For example, in $[Mo(C \equiv CPh)(CO)(dppe)Cp^*]$, **5b**, the *trans* angles differ by more than 40° [140.9° vs 97.6°], whereas in *trans*- $[Mo(C \equiv CPh)(CO)(PMe_3)_2Cp^*]$, **8b**, the difference is less than 1° [117.9° vs 117.0°]. A similar trend is observed for the halide derivatives **1a** and **4b**', although here the difference in *trans* angles for **4b**' is rather larger. The dppe alkynyl complexes **5b** and **6a/b** therefore exhibit a much larger distortion in molecular geometry away from the pseudo- $C_{4\nu}$ symmetry of a four-legged piano stool toward $C_{2\nu}$ than the related *trans*-PMe₃ systems **8a/b** and **9b**. Considering now the Cp°-Mo-(Ligand) or θ parameters, a variation in the approximate range 104–141° is observed. Specific ligands can adopt θ values over a significant



Figure 3. Plot of the molecular structure of 8a showing the atomlabeling scheme.



Figure 4. Plot of the molecular structure of 8b showing the atomlabeling scheme.

range dependent on the trans ligand and electron configuration, but in general, large θ parameters (typically 120–130°) are exhibited by good acceptor ligands such as CO or PR₃, whereas σ - or σ - $/\pi$ - donor ligands such as halide and C=CR normally have rather smaller θ values (typically 105–120°).²² The rationalization for these observations is intimately connected with electronic structure,^{22,23} and this will be reviewed at a later point in the paper. However, a feature of the alkynyl complexes 5b, 6a/b, 8a/b, and 9b is the combination of a double-faced π -acceptor ligand (CO) with a good σ/π -donor ligand (C=CR) in *cis* or *trans* arrangements, respectively. The salient θ parameters presented in Table 4 concern $\theta(X')$ and $\theta(P_{cis})$ (i.e., the phosphorus located *trans* to the CO ligand) for the dppe alkynyl complexes 5b and 6a/b. In particular for the Cp^{*} derivatives **5b** and **6b**, the small θ (C=CR) and large $\theta(P_{cis})$ angles lie close to the outer limits of observed values for [ML₄Cp'] and indicate a significant distortion away from the parent pseudo- $C_{4\nu}$ molecular symmetry.

Electrochemistry. To commence investigations on the redox chemistry of $[Mo(C \equiv CR)(CO)(L_2)Cp']$, the cyclic voltammetry of complexes **5b**, **6a/b**, **8a/b**, and **9b** at a glassy carbon electrode in CH₂Cl₂/0.2 M $[Bu^n_4N]$ PF₆ was examined; previous electrochemical studies on cyclopentadienyl molybdenum alkynyl complexes are restricted to the tricarbonyl derivatives $[Mo(C \equiv CPh)(CO)_3$ -Cp'].²⁵ The results are presented in Table 5, alongside data for the corresponding halide complexes $[MoX(CO)(L_2)Cp']$, which have been included for comparison.



Figure 5. Plot of the molecular structure of 7b showing the atomlabeling scheme. Key bond lengths (Å) and angles (deg): Mo(1)-C(1)2.137(4); C(1)-C(2) 1.198(6); Mo(1)-C(19) 1.953(5); Mo(1)-C(20) 1.969(5); Mo(1)-P(1) 2.451(1); C(1)-Mo(1)-P(1) 74.0(1); C(1)-Mo(1)-C(19) 74.7(2); C(1)-Mo(1)-C(20) 126.1(2); P(1)-MoC(19) 113.0(2); P(1)-Mo(1)-C(20) 76.8(2).

Under the conditions given in Table 5, each of the complexes undergoes a diffusion-controlled, chemically reversible, oneelectron oxidation with the separation between cathodic and anodic peak potentials comparable to that determined for the internal ferrocene standard. The electrochemistry of the majority of the halide complexes 1 to 4 has been reported previously,^{10,13,26} and the literature data are included in Table 5, but $E_{1/2}$ values were redetermined in the current work to provide a self-consistent set of values for comparison with the alkynyl analogues. A second irreversible oxidation was observed at higher potentials, as described previously for *trans*-[MoCl(CO)(PMe₃)₂Cp^{*}], **4b**;¹³ the potential for this process is reported as $E_p(A)$ in Table 5, determined at a scan rate of 100 mV s⁻¹.

The $E_{1/2}$ values for the first oxidation of $[MoX'(CO)(L_2)Cp']$ show a dependence upon X', L2, and Cp'. Consideration of [MoCl(CO)(dppe)Cp], 1a, and *trans*-[MoCl(CO)(PPh₃)₂Cp], 3a, suggests that the *trans*-phosphine arrangement of 3a leads to a reduction in $E_{1/2}$ of approximately 40 mV. Similarly, the replacement of Cp by Cp^{*} results in a shift of $E_{1/2}$ to negative potential by approximately 100 mV, although the magnitude of the change is slightly larger for the dppe series of complexes. Comparison of the halide/phenyl-alkynyl pairs [MoX'(CO)-(dppe)Cp (1a with 5a) and trans- $[MoX'(CO)(PMe_3)_2Cp^*]$ (4b with 8b) demonstrates that $E_{1/2}$ is shifted slightly negative by the replacement of Cl by C≡CPh; a similar trend is observed for $[MoX'(dppe)(\eta-C_7H_7)]$ (*E*_{1/2} (V) vs FeCp₂/[FeCp₂]⁺ in CH_2Cl_2 ; X' = Cl, -0.61 V; X' = C=CPh, -0.72 V). However, this feature is not reproduced in the $[MoX'(CO)(dppe)Cp^*]$ series, for which the alkynyl complexes 5b and 6b are slightly harder to oxidize than the chloride analogue 1b; this result may indicate an enhanced alkynyl contribution to the redox orbital in these examples. The absolute magnitudes of the $E_{1/2}$ values for the bis-phosphine alkynyl complexes 5a/b, 6a/b, 8a/b, and 9b lie intermediate between the potentials for [Ru(C=CPh) $(dppe)Cp^*]$ (-0.16 V vs FeCp₂/[FeCp₂]⁺ in CH₂Cl₂), in which the redox process features a substantial contribution from the alkynyl ligand,^{5a} and $[Mo(C \equiv CPh)(dppe)(\eta - C_7H_7)]$ and $[Fe(C \equiv CPh)$ (dppe)Cp*] $(-0.72, -0.61 \text{ V vs } \text{FeCp}_2/[\text{FeCp}_2]^+ \text{ in } \text{CH}_2\text{Cl}_2, \text{ respectively})$, in which the redox process is strongly metal based.^{3a,7a}

Spectroelectrochemical Analysis. To probe further the character of the redox orbital in the alkynyl complexes

Table 4.	Analysis	of Angular	Parameters in	[MoX'((CO)(I	L_2)Cp ⁷]	(X' =	= Cl or C≡CR	$)^a$
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	geometric trans angles (deg)					Cp°-M	o–(Ligand) (deg	g)
complex	X'-Mo-P _{trans}	P _{cis} -Mo-CO	X'-Mo-CO	P _{cis} -Mo-P _{cis}	$\theta(\mathbf{X}')$	$\theta(CO)$	$\theta(P_{trans})$	$\theta(P_{cis})$
5b	140.91(7)	97.60(8)			104.0	120.4	115.1	141.3
6a	136.0(2)	108.0(3)			106.9	125.0	116.8	126.3
6b	134.8(1)	104.4(1)			105.0	120.6	120.2	133.4
1a	142.4(2)	113.7(5)			106.8	121.5	110.2	124.8
8a			115.0(2)	123.24(6)	118.2	126.8		117.0, 119.3
8b			117.9(1)	116.97(3)	121.1	121.0		121.0, 121.9
9b			121.61(9)	113.79(2)	114.4	124.0		123.1, 122.6
4b'			130.4(2)	116.6(1)	111.9	117.8		121.2, 122.1
^a Definitions of P_{transv} P_{cis} as in Table 3.								

Table 5. Cyclic Voltammetric Data for $[MoX(CO)(L_2)Cp']$ (X' = halide, C=CR; L₂ = 2 PMe₃ or dppe; Cp' = Cp, Cp*)^{*a*}

compound	$E_{1/2}$ (V) (this work)	$E_{\rm p}({\rm A})~({\rm V})$	$E_{1/2}$ (V) (literature)
1a	-0.24	0.69	$-0.25^{b}(26)$
1b	-0.46	0.48	$-0.44^{c}(10)$
2a	-0.23	0.72	$-0.24^{b}(26)$
3a	-0.28	0.83	
4b	-0.54	0.75	$-0.48^{c}(10)-0.54^{b}(13)$
5a	-0.29	0.53	
5b	-0.41	0.45	
6a	-0.31	0.42	
6b	-0.44	0.48	
8a	-0.48	0.45	
8b	-0.56	0.61	
9b	-0.57	0.55	

^{*a*} All potentials are reported with reference to the FeCp₂/[FeCp₂]⁺ couple ($E_{1/2} = 0.00$ V). Experimental conditions (this work): 0.2 M [Buⁿ₄N]PF₆/CH₂Cl₂ solutions at a glassy carbon working electrode. $E_{\rm p}(A)$ = irreversible oxidation, at 100 mV s⁻¹. ^{*b*} In CH₂Cl₂. ^{*c*} In thf.

 $[Mo(C \equiv CR)(CO)(L_2)Cp']$, the spectroscopic properties of the 17-electron Mo(III) radical cations $[Mo(C \equiv CR)(CO)]$ $(L_2)Cp']^+$ invite examination. One approach to this objective is the direct chemical synthesis and isolation of the required radicals as achieved for $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]^+$, $[Fe(C \equiv CR)(dppe)Cp^*]^+$, and $[MoCl(CO)(L_2)Cp^*]^+$ (L₂ = dppe, 2PMe₃). Reaction of representative examples of [Mo- $(C \equiv CR)(CO)(L_2)Cp']$ with one equivalent of $[FeCp_2]PF_6$ in solution in cold (-40 °C) CH₂Cl₂ resulted in an immediate color change to deep turquoise-blue. However on slow warming to ambient temperature, the blue coloration faded to brown, and monitoring by solution IR spectroscopy revealed only decomposition products. The exception to these observations was 17electron *trans*- $[Mo(C \equiv CC_6H_4-4-Me)(CO)(PMe_3)_2Cp^*]^+$, $[9b]^+$, which persisted in solution for several minutes at room temperature; this derivative therefore defines the variables (R = C_6H_4 -4-Me; $L_2 = trans-(PMe_3)_2$; $Cp' = Cp^*$) conferring optimum stability to the radical cations $[Mo(C \equiv CR)(CO)(L_2)]$ -Cp']⁺. In view of the relatively poor thermal stability of the 17electron complexes $[Mo(C \equiv CR)(CO)(L_2)Cp']^+$, the synthetic studies were discontinued and the generation and observation of the radicals by spectroelectrochemical methods pursued.

Spectroelectrochemical investigations permit the convenient and rapid collection of spectroscopic data from each member of a

Table 6. Infrared Spectroscopic Data (cm^{-1}) for the Complexes $[MoX'(CO)(L_2)Cp']^{n+}$ $(n = 0 \text{ or } 1; X' = Cl \text{ or } C \equiv CR; L_2 = 2 \text{ PMe}_3 \text{ or dppe, } Cp' = Cp \text{ or } Cp^*)$

	<i>n</i> =	0	<i>n</i> =	n = 1		
	ν(CO)	$\nu(C\equiv C)$	ν(CO)	$\nu(C\equiv C)$	$\Delta \nu(\rm CO)$	$\Delta \nu(C \equiv C)$
1a ^a	1847 (1853)		2013 (2002)		166 (149)	
$\mathbf{1b}^{a}$	1822 (1835)		1981 (1971)		159 (136)	
4b ^{<i>a</i>}	1776 (1782)		1929 (1920)		153 (138)	
$5\mathbf{b}^b$	1828	2065	1969	2021	141	-44
6b ^b	1828	2068	1971	2012	143	-56
$\mathbf{8b}^{b}$	1776	2056	1931	2045	156	-11
9b ^b	1772	2056	1931	2047	159	-9

^{*a*} Data recorded in CH_2Cl_2 by generation of radicals *in situ* with [FeCp_2]PF₆ or (shown in parentheses) on isolated samples in thf.¹⁰ ^{*b*} Spectroelectrochemical measurement in 0.1 M [Buⁿ₄N]PF₆/CH₂Cl₂.

redox-related family of compounds.²⁷ In the case of metal alkynyl complexes, the characteristic, IR-active $\nu(C \equiv C)$ band reflects a convolution of σ/π -donation, π -back-bonding, and physical/kinematic effects. Nevertheless, the changes in $\nu(C \equiv C)$ that occur as a result of a redox change within a series of closely related alkynyl complexes can be used to assess the degree of involvement of the alkynyl ligand in the redox orbital,^{4a,b,28} especially when coupled with observation of other IR-active bands elsewhere in the molecule.^{6c,29} In the case of [Mo- $(C \equiv CR)(CO)(L_2)Cp']^{n+}$ in addition to the $\nu(C \equiv C)$ band, the $\nu(CO)$ band offers a spectroscopic handle not available to analogous studies on the d⁶ systems [Mo($C \equiv CR$)(dppe)- $(\eta$ - C_7H_7)]ⁿ⁺ and [M($C \equiv CR$)(dppe)Cp*]ⁿ⁺ (M = Fe or Ru).

Guided by the results of the cyclic voltammetry, an IR spectroelectrochemical investigation was carried out on the bisphosphine alkynyl complexes 5a/b, 6a/b, 8a/b, and 9b. The 17-electron radicals formed from the Cp complexes 5a, 6a, and 8a proved to be too reactive to be accessible to room-temperature, spectroelectrochemical investigations. However the radicals derived from the Cp* analogues 5b, 6b, 8b, and 9b exhibited enhanced stability, sufficient for study in the spectroelectrochemical cation (and hence the validity of $\nu(CO)$ and $\nu(C \equiv C)$ data) was established by back-reduction, which resulted predominantly in recovery of the IR spectrum assigned to the 18-electron precursor, although small quantities of secondary products were also observed. The IR data obtained and the shifts in carbonyl and alkynyl stretching



Figure 6. IR spectra of $\mathbf{8b}/[\mathbf{8b}]^+$ generated *in situ* using spectroelectrochemical methods (CH₂Cl₂/0.1 M [Buⁿ₄N]PF₆); — = $\mathbf{8b}$ (with trace of $[\mathbf{8b}]^+$ also present); ---- = $[\mathbf{8b}]^+$.

frequencies resulting from one-electron oxidation $[\Delta\nu(CO)]$ and $\Delta\nu(C\equiv C)$, respectively] are summarized in Table 6, and the experimental spectra obtained for the redox pair *trans*-[Mo- $(C\equiv CPh)(CO)(PMe_3)_2Cp^*]^{n+}$, **8b**/[**8b**]⁺, are presented in Figure 6. Data for the related chloride complexes $1a/[1a]^+$, $1b/[1b]^+$, and $4b/[4b]^+$ are also included to provide a direct comparison of the $\Delta\nu(CO)$ parameter. These latter data are either literature values, recorded on isolated samples of the radicals in thf,¹⁰ or values obtained in the current work in CH₂Cl₂ (to allow direct comparison with alkynyl analogues) in which green-brown solutions of the radicals $[1a]^+$, $[1b]^+$, and $[4b]^+$ were generated *in situ* by addition of [FeCp₂]PF₆ to solutions of the 18-electron precursors. It became clear from these investigations that the halide radicals $[MoCl(CO)(L_2)Cp']^+$ are significantly more stable than their alkynyl counterparts.

One-electron oxidation of all complexes of the type [MoX'- $(CO)(L_2)Cp'$ (X' = Cl or C=CR) results in a shift in $\nu(CO)$ to higher wavenumber by $140-160 \text{ cm}^{-1}$, indicative of significant metal character in the redox orbital in all cases.³⁰ However, a slightly smaller shift in $\nu(CO)$ is observed for the alkynyl complexes $[Mo(C=CR)(CO)(dppe)Cp^*]$, **5b** and **6b**, a feature of significance when considered together with shifts in $\nu(C \equiv C)$; see below. A more direct measure of the extent of the alkynyl contribution to the redox orbital is provided by the shift in $\nu(C \equiv C)$ following one-electron oxidation. For example the magnitude of $\Delta \nu$ (C=C) resulting from the metal centered, oneelectron oxidation of $[Mo(C \equiv CPh)(dppe)(\eta - C_7H_7)](-13 \text{ cm}^-)$ in $CH_2Cl_2)^{7a}$ contrasts with the corresponding parameter of $-143 \text{ cm}^{-1} (CH_2Cl_2)$ observed for oxidation of $[Ru(C \equiv CPh)]$ (dppe)Cp*], where the redox process results in significant depopulation of the alkynyl π -bonding orbitals.^{4a} The key $\Delta \nu (C \equiv C)$ parameter was not readily determined for all complexes of formulation $[Mo(C \equiv CR)(CO)(L_2)Cp']^{n+}$ because of overlap of $\nu(C \equiv C)$ and $\nu(CO)$ stretches in the 17-electron radicals, a problem compounded by reduction in the intensity of the $\nu(C \equiv C)$ band in the oxidized products. However, in the case of the Cp* complexes selected for investigation, determination of $\Delta \nu$ (C=C) was facilitated by the

lower wavenumber for ν (CO) intrinsic to the Cp^{*} derivatives. In all cases considered, the magnitude of $\Delta \nu$ (C=C) is relatively small, with a maximum value of -56 cm^{-1} observed for [Mo(C=CC₆H₄-4-Me)(CO)(dppe)Cp*], 6b. However, the results in Table 6 show that the size of the negative shift in $\nu(C \equiv C)$ resulting from one-electron oxidation is molecular geometry dependent. Thus in the dppe complexes **5b** and **6b**, the shift in $\nu(C \equiv C)$ (in the range -44 to -56 cm⁻¹ for the alkynyl R substituents selected) is similar to that found for $[Fe(C \equiv CR)(dppe)Cp^*]^{n+}$ for equivalent R substituents.^{3a} By comparison a much smaller change in $\nu(C \equiv C)$ is observed for the *trans*-PMe₃ derivatives **8b** and **9b** (ca. -10 cm^{-1}), more comparable⁷ to the behavior of $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]^{n+}$. Taken together the $\Delta \nu$ (CO) and $\Delta \nu$ (C=C) data suggest that the redox orbital in the complexes $[Mo(C \equiv CR)(CO)(L_2)Cp']$ is strongly metal based but with some alkynyl character, particularly in the dppe complexes 5b and 6b.

Previous investigations on the UV-visible spectra of metal alkynyl complexes $[Fe(C \equiv CR)(dppe)Cp^*]^{n+}$ and $[Mo(C \equiv CR)(dppe)(\eta)$ $(C_7H_7)^{n+}$ (n = 0 or 1) have demonstrated ^{3b,7a} the operation of charge transfer bands involving the alkynyl ligand with excitation energies in the visible region. In the neutral 18-electron complexes these are MLCT bands with energies at the blue end of the visible region, whereas in the 17-electron radicals, strong LMCT bands are observed with energies around 18 000 cm⁻¹ (550 nm) giving rise to a deep green or blue coloration. The intense turquoise-blue color of solutions of the 17-electron radicals formed at low temperature in the preliminary synthetic investigations on [Mo(C≡CR)(CO)(L₂)Cp']⁺ suggested that analogous charge transfer processes may occur in these complexes. To investigate further, the UV-visible spectra of the Cp* alkynyl complexes **5b**, **6b**, **8b**, and **9b** and the corresponding radicals were recorded using spectroelectrochemical methods; the experimental spectra for trans- $[Mo(C \equiv CC_6H_4-4-Me)(CO)(PMe_3)_2Cp^*]^{n+1}$ $9b/ [9b]^+$, are illustrated in Figure 7, with all data summarized in Table 7.

The key feature in the spectroelectrochemically generated UV-visible spectra of $5b/[5b]^+$, $6b/[6b]^+$, $8b/[8b]^+$, and $9b/[9b]^+$ is the appearance of a new band in the visible region

in the spectra of the 17-electron radicals ($[5b]^+$, 15 800 cm⁻¹, 633 nm; $[6b]^+$, 15 770 cm⁻¹, 634 nm; $[8b]^+$, 16 700 cm⁻¹, 599 nm; and $[9b]^+$, 16 000 cm⁻¹, 625 nm). Similar absorptions in the visible region of 17-electron alkynyl complexes have been reported previously (for example $[Mo(C \equiv CPh)(dppe)(\eta - C_7H_7)]^+$, 16 900 cm⁻¹, 592 nm)^{7a} and assigned with the aid of a TD-DFT treatment to an alkynyl-to-metal LMCT process.

EPR Investigations. The 17-electron radicals $[MoX'(CO)(L_2)-$ Cp']⁺ (X' = halide or C=CR) were further investigated by X-band solution EPR spectroscopy in CH₂Cl₂. Previous work on the EPR spectra of isolated samples of the chloride derivatives [MoCl- $(CO)(dppe)Cp]^+$, $[1a]^+$, $[MoCl(CO)(dppe)Cp^*]^+$, $[1b]^+$, and *trans*- $[MoCl(CO)(PMe_3)_2Cp^*]^+$, $[4b]^+$, recorded in solution in thf reports isotropic spectra with resolved hyperfine coupling to ⁹⁵⁷⁹⁷Mo and ³¹P.¹⁰ In the current investigation, samples of the 17electron radicals were generated by in situ oxidation with [FeCp2]-PF₆ in CH₂Cl₂ followed by immediate cooling to 243 K. These modified conditions allowed observation of the full range of radical cations, including the unstable alkynyl Cp complexes. Additionally, enhanced spectral resolution was obtained leading in the case of $[MoCl(CO)(dppe)Cp]^+$, $[1a]^+$, to the observation of hyperfine coupling both to the Cl ligand and to H of the Cp ring. A sample of $[1a]^+$ was also generated from 1a and $[FeCp_2]PF_6$ in thf. The resulting EPR spectrum was almost identical to that reported for an isolated sample of $[1a]^+$ and to the spectrum obtained in CH_2Cl_2 except that the hyperfine couplings to Cl and H of the Cp ring were now unresolved. A full analysis of the EPR spectral parameters, confirmed by spectral simulation, is presented in Table 8.

The solution EPR spectra of the dppe halide derivatives $[1a]^+$, $[1b]^+$, and $[2a]^+$ exhibit excellent resolution of hyperfine couplings, as shown in Figure 8a–c, respectively. For $[1a]^+$ and $[1b]^+$, the underlying spectral pattern is a doublet of doublets due to coupling to the inequivalent phosphorus atoms of the



Figure 7. UV–visible spectra of $9b/[9b]^+$ generated *in situ* by spectroelectrochemical methods (CH₂Cl₂/0.1 M [Buⁿ₄N]PF₆).

dppe ligand and a series of satellites from the spin-active molybdenum isotopes ⁹⁵Mo and ⁹⁷Mo. The hyperfine couplings to ${}^{95/97}$ Mo and 31 P are in close agreement with those previously reported and similar to those determined for the related complex $[MoCl(dppe)(\eta-C_7H_7)]^+$ (a_{iso} , G, CH₂Cl₂ solution, 243 K: Mo, 40.0; ³¹P, 23.2) in which the unpaired electron is strongly metal centered.³¹ Additional hyperfine interactions, superimposed upon the basic pattern, are clearly evident in Figure 8a,b. For the Cp^{*} complex $[1b]^+$, the spectrum can be simulated by inclusion of additional hyperfine coupling to ³⁵Cl/³⁷Cl, but for [1a]⁺, the spectrum exhibits further complexity arising from hyperfine coupling to the hydrogens of the Cp ring, a feature also observed in the EPR spectrum of the 17-electron radical $[Mo(dppe)_2Cp]^{2+,32}$ The EPR spectrum of the bromide derivative $[2a]^+$ (Figure 8c) confirms the contribution of the halide ligand, but in this case, the much larger hyperfine coupling to Br (12.5 G) leads to significant perturbation of the spectral pattern.

The key spectral feature of the *trans*-phosphine chloride complexes $[MoCl(CO)(PPh_3)_2Cp]^+$, $[3a]^+$, and $[MoCl(CO)(PMe_3)_2Cp^*]^+$, $[4b]^+$, is a 1:2:1 triplet confirming that the *trans*-phosphine geometry is retained in the 17-electron radicals. In addition to hyperfine coupling to $^{95/97}Mo$ and ^{31}P , superimposed coupling to Cl (and in $[3a]^+$, H of the Cp ring) was also observed albeit with poorer resolution than for the dppe complexes. The hyperfine values computed for *trans*- $[MoCl(CO)(PR_3)_2Cp']^+$ appear almost invariant with the identity of PR₃ and Cp', although $a_{iso}(Mo)$ values are approximately 3 G smaller than for the corresponding dppe complexes.

The EPR spectra of the alkynyl cyclopentadienyl complexes $[Mo(C \equiv CR)(CO)(dppe)Cp]^+$ (R = Ph, $[Sa]^+$, R = C_6H_4 -4-Me, $[Ga]^+$) are similar to the spectrum of the chloride analogue $[1a]^+$,

Table 8	B. EPR	Data f	for the	17-Ele	ectron	Radicals
MoX'(CO)(L	$_{2})Cp'$	$]^{+}.^{a}$			

	$g_{\rm iso}/$	$a_{\rm iso}({ m Mo})/$	$a_{\rm iso}(^{31}{\rm P}_1)/$	$a_{\rm iso}(^{31}{\rm P}_2)/$	$a_{\rm iso}({\rm other})/$
	G	G	G	G	G
[1a]+	1.996	31.0	27.9	14.3	1.9, 1.6 (Cl), 2.2 (H, Cp)
[1b] ⁺	1.999	31.0	27.9	18.3	1.9, 1.6 (Cl)
$[2a]^+$	2.019	25.5	27.0	15.0	12.5 (Br)
$[3a]^{+}$	1.998	28.5	18.0	18.0	1.1, 1.4 (Cl), 2.6 (H, Cp)
$[4b]^{+}$	1.998	27.5	24.0	24.0	
$[5a]^+$	1.999	26.4	23.8	14.4	
$[5b]^{+}$	1.997	15.5	20.5	6.0	
[6a]+	1.999	26.0	23.6	14.0	
[6b] ⁺	1.998	15.8	20.2	5.8	
[8a]+	2.005	25.0	20.0	20.0	
[8b] ⁺	2.001	26.0	25.2	25.2	
[9b] ⁺	2.001	26.0	25.2	25.2	

 a X-band solution spectra in $\rm CH_2Cl_2$ at 243 K; hyperfine couplings in Gauss.

Table 7. UV–Visible Data for the Complexes $[Mo(C \equiv CR)(CO)(L_2)Cp^*]^{n+}$ $(n = 0 \text{ or } 1)^a$

complex	n = 0	n = +1
5b	42 500 (29 000), 29 200 (11 200), 22 400, sh, (1300)	42 500 (29 000), 33 100, sh, (10 700), 25 000 (2500), 15 800 (1800)
6b	30 500 (12 160)	15 770 (1370)
8b	40 300, br, (13 960), 29 400 (10 540), 26 320, sh, (5460)	35 700 (11 500), 23 400 (2430), 16 700 (1700)
9b	40 500 (14 500), 29 100 (9200), 24 800, sh, (3100)	42 200 (14 700), 35 500 (11 100), 25 900 (1700), 23 400 (1800), 16 000 (1500)
$^{a} \nu_{\rm max}/{\rm cm}^{-1}$	$(\varepsilon/M^{-1} \text{ cm}^{-1})$ determined by spectroelectrochemical met	hods in 0.1 M $[Bu_4^n N]PF_6/CH_2Cl_2$.



Figure 8. Fluid solution (CH₂Cl₂, 243 K), second derivative X-band EPR spectra of (a) [MoCl(CO)(dppe)Cp]PF₆ [1a]PF₆; (b) [MoCl(CO)-(dppe)Cp^{*}]PF₆ [1b]PF₆; and (c) [MoBr(CO)(dppe)Cp]PF₆ [2a]PF₆.

although no hyperfine coupling to H of the Cp ring was observed and hyperfine couplings to ${}^{95/97}$ Mo and 31 P are slightly smaller. However, substitution of Cp by Cp* produces a dramatic effect with very significant reduction in a_{iso} (Mo) and a_{iso} (P), as evident from a comparison of Figure 9a and b. Thus, in the Cp* complexes [Mo(C=CR)(CO)(dppe)Cp*]+, [**5b**]⁺ and [**6b**]⁺, a_{iso} (Mo) and the averaged value of a_{iso} (P) are approximately one-half of the corresponding parameters both for the Cp* chloride derivative [**1b**]⁺ and in the Cp alkynyl analogues [**5a**]⁺ and [**6a**]⁺. Of particular note is the very small hyperfine (ca. 6 G) to one of the phosphorus nuclei in the Cp* alkynyl systems [**5b**]⁺ and [**6b**]⁺; this effect is observed only for the combination of variables Cp' = Cp*, X' = C==CR in [MoX'(CO)(dppe)Cp']⁺. The reduced hyperfine couplings to Mo and phosphorus in the pentamethylcyclopentadienyl alkynyl complexes [**5b**]⁺ and [**6b**]⁺ may be indicative of enhanced delocalization of spin density onto the alkynyl ligand.

In contrast with the dppe alkynyl complexes, the EPR spectra of the PMe₃ alkynyl complexes *trans*- $[Mo(C \equiv CR)(CO)-(PMe_3)_2Cp']^+$ ($[8a]^+$ and its Cp* analogues $[8b]^+$ and $[9b]^+$)

were almost identical to the chloride derivatives $[3a]^+$ and $[4b]^+$. The principal 1:2:1 triplet pattern arising from hyperfine coupling to two equivalent PMe₃ ligands was observed, confirming retention of the *trans*-PMe₃ geometry in the alkynyl radicals. However, unlike the dppe complexes, the changes in $a_{iso}(Mo)$ and $a_{iso}(P)$ resulting from exchange of Cl for C=CPh or Cp* in place of Cp are very small.

Electronic Structure Calculations. The experimental investigations outlined above suggest that the redox orbital in $[Mo(C \equiv CR)(CO)(L_2)Cp']$ has substantial metal-centered character, evident from the large increase in $\nu(CO)$ following one-electron oxidation to the 17-electron radicals and the correspondingly rather small negative shift in $\nu(C \equiv C)$. However, EPR investigations on $[MoX'(CO)(L_2)Cp']^+(X' = halide$ or C≡CR) indicate some spin delocalization onto the X' ligand, either from the direct observation of $a_{iso}(Cl/Br)$ in the halide radicals $[MoX'(CO)(L_2)Cp']^+$ or indirectly via the reduced magnitude of the hyperfine couplings, $a_{iso}(^{95/97}Mo)$ and $a_{iso}^ (^{31}P)$ in the Cp^{*} alkynyl complexes $[5b]^+$ and $[6b]^+$. Moreover the two series of complexes $[Mo(C \equiv CR)(CO)(dppe)Cp']^{n+}$ and *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']^{n+}$ exhibit distinctive structural and spectroscopic characteristics with evidence for enhanced participation of the alkynyl ligand in the redox orbital of the dppe systems.

To rationalize these observations in terms of the electronic structure of $[Mo(C \equiv CR)(CO)(L_2)Cp']$, a computational study was conducted at the DFT level using the B3LYP functional and the def-SVP basis set; this level of theory was used to provide consistency with previous investigations on $[M(C \equiv CPh)(dppe)(\eta-C_7H_7)]^{n+}$ ($M = Mo^{7a}$ or W^8). For purposes of computational efficiency, the model systems $[Mo(C \equiv CPh)(CO)(dHpe)Cp]$, **5-H** (dHpe = H₂PCH₂CH₂PH₂), and *trans*-[Mo-(C \equiv CPh)(CO)(PH_3)_2Cp], **8-H**, were investigated as the closed-shell, 18-electron complexes. The calculated complexes are denoted -H to distinguish computational and experimental systems.

Key bond length and angle parameters from the DFT-optimized geometries of complexes **5-H** and **8-H** are summarized in Table 9. The calculated structural data, including *trans* angles across the tetrapodal ligand set, are in good agreement with the crystallographically determined structures of the related experimental systems [Mo($C \equiv CC_6H_4$ -4-Me)(CO)(dppe)Cp], **6a** (given in place of the phenyl-alkynyl derivative **5a**, for which X-ray data are not available), and *trans*-[Mo($C \equiv CPh$)(CO)(PMe₃)₂Cp], **8a**, respectively. The energies and composition of the principal frontier orbitals (LUMO, HOMO, HOMO–1, and HOMO–2) are shown in Table 10, and plots of these orbitals for **5-H** and **8-H** are presented in Figures 10 and 11, respectively.

The electronic structures of the two model systems $[Mo(C \equiv CPh)(CO)(dHpe)Cp]$, **5-H**, and *trans*- $[Mo(C \equiv CPh)(CO)-(PH_3)_2Cp]$, **8-H**, appear strikingly different. This is a direct consequence of the *cis* versus *trans* molecular geometry of the two systems and not a result of the identity of the P-donor ligands since calculations on the computational model species *cis*- $[Mo-(C \equiv CPh)(CO)(PH_3)_2Cp]$ reveal an electronic structure analogous to that of the dHpe complex **5-H**. In both **5-H** and **8-H**, a key aspect of electronic structure [not encountered for the widely reported tripodal alkynyl complexes $[M(C \equiv CPh)(dppe)(\eta-L)]$ (M = Fe, Ru, L = Cp; M = Mo, $L = C_7H_7$)] involves the bonding interactions between filled metal d-orbitals and the empty CO π^* -level. The different molecular geometries of **5-H** and **8-H**



Figure 9. Fluid solution (CH₂Cl₂, 243 K), second derivative X-band EPR spectra of (a) $[Mo(C \equiv CC_6H_4-4Me)(CO)(dppe)Cp]PF_{69}$ [6a]PF₆₉ and (b) $[Mo(C \equiv CC_6H_4-4Me)(CO)(dppe)Cp^*]PF_{69}$ [6b]PF₆₉.

with the CO π^* -orbitals, and this is reflected in the resulting electronic structures.

The electronic structure of the more straightforward case, the trans-PH₃ complex 8-H, is considered first; the principal components of the frontier orbitals are illustrated in Figure 11. The HOMO of 8-H features the metal d_{z^2} -orbital, and therefore the local symmetry is defined with the z axis coincident with a line between the metal and the centroid of the cyclopentadienyl ring. This arrangement of the d-orbital manifold, in which d_{xy} contributes to the HOMO-1 (just slightly lower in energy than the d_{z^2} -based HOMO) and d_{yz} - and d_{xz} -orbitals are involved in π -bonding interactions with the e₁-level of the Cp ligand (identified as HOMO-6 and HOMO-14, respectively, in Figure 11), is consistent with previous theoretical treatments for four-leg piano stool systems.^{23,33} The HOMO of 8-H is strongly metal centered (59%) with significant components on CO (16%) and C_{β} of the alkynyl ligand (12%). The principal metal-ligand interactions are bonding to the CO ligand and a filled—filled, antibonding interaction with the alkynyl π -orbital; these filled-filled overlaps are a recurrent feature of the HOMOs of electron-rich metal alkynyl systems.^{3b,4a,7a} However in 8-H the poor symmetry match of the alkynyl π -orbital with the metal d_{z²}orbital, combined with a competing bonding overlap with the CO π^* -level, prescribes only a weak metal alkynyl interaction. In HOMO-1, the d_{xy} -orbital similarly serves a dual function of a bonding overlap with the CO π^* -orbital and a filled-filled

Table 9. Selected Bond Lengths (Å) and Angles (deg) for the
Calculated Systems $[Mo(C \equiv CPh)(CO)(L_2)Cp]$, 5-H and
8-H, and Experimental Counterparts 6a and 8a ^a

	5-H	6a	8-H	8a				
$Mo-C_{\alpha}$	2.141	2.134(9)	2.148	2.129(6)				
$C_{\alpha}-C_{\beta}$	1.232	1.21(1)	1.235	1.221(9)				
Mo-P	2.460,	2.428(2),	2.447,	2.423(2),				
	2.456	2.467(2)	2.447	2.426(2)				
Mo-CO	1.970	1.97(1)	1.955	1.923(6)				
P _{cis} -Mo-P _{cis}			120.3	123.23(6)				
C_{α} -Mo-CO			117.7	115.0(2)				
P _{cis} -MoCO	105.8	108.0(3)						
C_{α} -Mo- P_{trans}	136.9	136.0(2)						
^a See Table 3 for key to atom-labeling scheme.								

Table 10. Energy and Composition of Frontier Orbitals in the Calculated Systems $[Mo(C \equiv CPh)(CO)(L_2)Cp]$, 5-H and 8-H

		energy	%	%	%	%	%	%	%
complex	orbital	(eV)	Mo	Ср	L_2	СО	C_{α}	C_{β}	Ph
5-H	LUMO	-0.81	35	15	30	7	4	5	5
	НОМО	-4.76	34	5	6	4	12	20	19
	HOMO-1	-5.01	52	5	9	13	5	12	4
	HOMO-2	-5.88	31	4	8	5	19	8	25
8-H	LUMO	-0.78	17	8	26	5	7	4	33
	НОМО	-4.91	59	3	6	16	2	12	1
	HOMO-1	-5.08	41	5	4	10	8	15	17
	HOMO-2	-6.15	25	2	10	7	19	5	32

antibonding interaction with the remaining alkynyl π -level; this latter interaction is more efficient in the *xy* plane, evident from much greater alkynyl contribution (40%) to the orbital composition. HOMO-2 (which is significantly lowered in energy with respect to HOMO-1 and almost 60% localized on the alkynyl ligand) involves metal—ligand bonding interactions with both the filled alkynyl π - and empty CO π^* -levels. The transfer of electron density from a filled alkynyl π -orbital to the empty π^* -level of the *trans*-CO ligand may be facilitated by the configuration of HOMO-2.

The frontier molecular orbitals of the *cis*-phosphine, dHpe complex **5-H** are shown in Figure 10. As for **8-H**, interactions with the filled alkynyl π - and empty CO π^* -orbitals dominate the composition of HOMO, HOMO-1, and HOMO-2, but the energy ordering of the d-orbital manifold appears to be very different, with d_{xy} replacing d_{z^2} as the frontier metal orbital contributing to the HOMO (assuming a common coordinate system in which the z direction is located along the metal-ring axis). However, further consideration shows that the electronic structure of **5-H** can be interpreted as a perturbation of the structure of **8-H**.

The HOMO of **5-H** comprises a filled-filled, antibonding overlap between the alkynyl π -level and the metal d_{xy} -orbital, equivalent to that observed in the HOMO-1 of **8-H**. This is a strong interaction, similar to that found in the HOMO of $[M(C \equiv CPh)(dppe)Cp]$ (M = Fe, Ru)^{3b,4a} and unconstrained by symmetry or competition with a *trans*-carbonyl ligand. Accordingly the HOMO of **5-H** has increased alkynyl character

Figure 10. LUMO, HOMO, HOMO-1, HOMO-2, HOMO-5, and HOMO-6 of 5-H at B3LYP/SVP plotted as isosurfaces of 0.04 au.

(51%) and reduced metal (34%) and CO (4%) composition by comparison with the HOMO of 8-H. The composition of HOMO-1 and HOMO-2 of 5-H is not readily defined in terms of simple metal d-orbital components, although the "on axis" z component of HOMO-1 pointing directly toward the Cp ring is easily recognized. As noted previously in the X-ray structural studies, the complexes $[Mo(C \equiv CR)(CO)(dppe)]$ Cp'] (5b and 6a/b), in which the P-donor atoms are disposed mutually cis, undergo a distortion of the molecular geometry away from the idealized $C_{4\nu}$ symmetry of a square-based pyramidal form toward $C_{2\nu}$, a feature reproduced in the calculated structure of 5-H. This reduction in molecular symmetry from pseudo- $C_{4\nu}$ to $C_{2\nu}$ permits significant mixing of the metal d_{z^2} - and $d_{x^2-y^2}$ -orbitals and, as previously proposed,²³ leads to the formation of two new hybrid orbitals, directed along the yz and xz axes, as manifest in HOMO-1 and HOMO-2 of Figure 10. Energetically, the driving force for a rehybridization in the dHpe system is the localization of metal orbitals in their interaction with strong acceptor (CO) or strong donor (C=CR) ligands. In HOMO-1, the acceptor ligands (CO and the phosphine located trans to CO), which are bent down away from the xy plane, experience enhanced metal-to-ligand π -back-bonding in the yz plane (evident from the 13% CO character of this orbital); this is the origin of the large θ values $[\theta(CO), \theta(P_{cis})]$ for these ligands, as shown in Table 4. By contrast in HOMO-2, the donor ligands (C=CR and the phosphine *trans* to the alkynyl ligand, P_{trans} in Table 4) are inclined upward toward the xy plane (small θ values) to optimize the bonding interaction between the filled

alkynyl π -orbital and the metal hybrid acceptor orbital directed in the *xz* plane. An important result of the rehybridization in **5-H** is that in HOMO-1 the metal—alkynyl interaction is nonbonding, thus avoiding the filled—filled antibonding interaction in the alternative electronic structure of **8-H**. An analogous rehybridization of the *trans*-phosphine complex **8-H** is not energetically favorable because the *trans*-disposed CO acceptor and C=CR donor ligands must share the same metal orbital.

The electronic structures outlined above provide the basis for an understanding of the redox behavior of the experimental systems with *cis*-phosphine (**5a/b** and **6a/b**) and *trans*-phosphine (**8a/b** and **9b**) molecular geometries. Although the HOMOs of both **5**-**H** and **8**-**H** are quite strongly metal centered (Table 10), the relative contribution of the alkynyl ligand in the dHpe system **5**-**H** is much greater than for the *trans*-PH₃ counterpart, **8**-**H** (metal: alkynyl % compositions, **5**-**H**: 34:51; **8**-**H**: 59:15). The reduced metal character and increased alkynyl composition of the HOMO of the dHpe complex **5**-**H** is consistent with the rather larger negative shift in $\nu(C\equiv C)$ resulting from one-electron oxidation of the experimental systems [Mo(C=CR)(CO)(dppe)Cp*] (**5b**, **6b**) by comparison with *trans*-[Mo(C=CR)(CO)(PMe_3)₂Cp*] (**8b**, **9b**).

Finally the poor thermal stability of the 17-electron alkynyl radicals $[Mo(C \equiv CR)(CO)(L_2)Cp']^+$ should be addressed. Given the small shifts in $\nu(C \equiv C)$ resulting from one-electron oxidation, especially for the *trans*-phosphine complexes, the difficulty in isolation of the 17-electron radical cations is surprising when compared with the cycloheptatrienyl complexes

LUMO (-0.78 eV)	HOMO (-4.91 eV) (d_{z^2})
HOMO-1 (-5.08 eV) (d _{xy})	HOMO-2 (-6.15 eV)
HOMO-6 (-7.43 eV) (d _{yz})	HOMO–14 (–10.43 eV) (d _{xz})

Figure 11. LUMO, HOMO, HOMO-1, HOMO-2, HOMO-6, and HOMO-14 of 8-H at B3LYP/SVP plotted as isosurfaces of 0.04 au.

[Mo(C≡CR)(dppe)(η -C₇H₇)]⁺, which are stable systems for a wide range of alkynyl substituents R.⁷ Two factors may contribute to the limited stability of [Mo(C≡CR)(CO)(L₂) Cp']⁺. First the cyclopentadienyl complexes incorporate a labile carbonyl ligand, which is activated to elimination or substitution by one-electron oxidation. However, this in itself cannot explain the rapid decomposition of the alkynyl radicals since the chloride analogues [MoCl(CO)(L₂)Cp^{*}]⁺, although reactive, are isolable.¹⁰ The additional function of the alkynyl ligand may be to facilitate a decomposition pathway, promoted by the formally Mo(III), d³ metal center, involving conversion of the σ-bonded alkynyl to a π -bonded fourelectron alkyne ligand, thus driving elimination of the CO ligand.

CONCLUSIONS

Synthetic routes to bis-phosphine-substituted cyclopentadienyl molybdenum alkynyl complexes $[Mo(C \equiv CR)(CO)(dppe)$ Cp'] and *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$ (R = Ph or C_6H_4 -4-Me, Cp' = Cp or Cp^*) have been developed. The new complexes have been characterized by a range of spectroscopic methods and representative examples investigated by X-ray structural studies, which reveal significant structural distortions away from pseudo- $C_{4\nu}$ symmetry in complexes of the type $[Mo(C \equiv CR)(CO)(dppe)Cp^*]$. Cyclic voltammetric investigations show that each of the complexes $[Mo(C \equiv CR)(CO)$ (dppe)Cp'] and *trans*- $[Mo(C \equiv CR)(CO)(PMe_3)_2Cp']$ undergoes a reversible one-electron oxidation on the electrochemical time scale. Although the resulting 17-electron radicals were too reactive for chemical isolation, further investigations by spectroelectrochemical IR and UV-visible techniques were accomplished for the more stable Cp^{*} derivatives. Changes in ν (CO) and $\nu(C \equiv C)$ resulting from one-electron oxidation provide a dual probe of the redox process, which is strongly metal based, as evidenced by shifts in $\nu(CO)$ to higher wavenumber, by 140– 160 cm⁻¹. However the response of ν (C=C) to one-electron oxidation differs between the two groups of complexes [Mo- $(C \equiv CR)(CO)(dppe)Cp^*]^{n+}$ and trans- $[Mo(C \equiv CR)(CO)$ - $(PMe_3)_2 Cp^*$ ^{*n*+} (*n* = 0 or 1), with the rather larger negative shift for $[Mo(C \equiv CR)(CO)(dppe)Cp^*]^{n+}$ indicative of greater alkynyl character in the redox orbital, a conclusion supported by the large reductions in hyperfine coupling to Mo and P observed in the solution EPR spectra of $[Mo(C \equiv CR)(CO)(dppe)Cp^*]^+$. DFT, electronic structure calculations on the model complexes $[Mo(C \equiv CR)(CO)(dHpe)Cp]$ and *trans*- $[Mo(C \equiv CR)(CO)$ - $(PH_3)_2Cp$ reveal a switch in electronic structure dependent on the complex coordination geometry. In *trans*- $[Mo(C \equiv CR)$ - $(CO)(PH_3)_2Cp$, the HOMO incorporates a symmetry-restricted antibonding interaction between the metal d_{z2}-orbital and the filled alkynyl π -orbital. By contrast in [Mo(C=-CR)(CO)(dHpe)Cp], a structural distortion leads to a HOMO with metal d_{xy} character and enhanced alkynyl contribution in accord with the properties of the experimental systems. This work indicates the potential for a switchable redox response, via a perturbation in electronic structure controlled by changes in molecular geometry.

EXPERIMENTAL SECTION

General Procedures. The preparation, purification, and reactions of the complexes described were carried out under dry nitrogen using standard Schlenk techniques. The complexes [MoCl(CO)₃Cp'] (Cp' = Cp, Cp^*)³⁴ and $[Mo(C \equiv CPh)(CO)_3 Cp']$ (Cp' = Cp, Cp^*)³⁵ were prepared by published procedures, and the alkynes HC=CPh and HC≡CC₆H₄-4-Me were purchased from commercial sources. NMR spectra were recorded from CDCl₃ solutions, unless otherwise stated, on Varian Inova 300 or 400 spectrometers at room temperature and referenced against solvent resonances (¹H, ¹³C) or external H₃PO₄ (³¹P). Infrared spectra were obtained on Perkin-Elmer FT RX1 or Nicolet Avatar spectrometers. Mass spectra were recorded using Thermo Quest Finnigan Trace GC/MS or Thermo Electron Finnigan LTQ FT mass spectrometers. MALDI mass spectra were recorded using a Micromass/Waters TOF Spec 2E instrument. Microanalyses were conducted by the staff of the Microanalytical Services of the School of Chemistry, University of Manchester. Cyclic voltammograms were recorded ($\nu = 100 \text{ mV s}^{-1}$) from 0.2 M [Buⁿ₄N]PF₆, CH₂Cl₂ solutions ca. 1×10^{-4} M in analyte using a three-electrode cell equipped with a glassy carbon disk working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode. All redox potentials are reported with reference to an internal standard of the ferrocene/ferrocenium couple (FeCp₂/[FeCp₂]⁺ = 0.00 V). UV-visible and IR spectroelectrochemical experiments were performed at room temperature with an airtight OTTLE cell of Hartl design^{27a} equipped with Pt minigrid working and counter electrodes, a Ag wire reference electrode, and CaF2 windows using either a Nicolet Avatar spectrometer or a Perkin-Elmer Lambda 900 spectrophotometer. EPR experiments were conducted on a Bruker BioSPin EMX microspectrometer at X-band (9 GHz); spectra were recorded at 243 K and are the average of 16 scans. Spectral analysis and simulation was carried out using Bruker WinEPR software (Bruker Biospin Ltd.).

Preparations. Preparation of [MoCl(CO)(dppe)Cp] (1a). A solution of [MoCl(CO)₃Cp] (2.40 g, 8.60 mmol), dissolved in hot toluene (100 cm^3) was added dropwise over a period of 90 min to a solution of dppe (3.70 g, 9.3 mmol) in refluxing toluene (50 cm^3) . After completion of the addition, reflux was continued for a further 3 h. Then the reaction mixture was evaporated to dryness. The residue, dissolved in CH₂Cl₂, was transferred to an n-hexane-alumina chromatography column, and the product eluted as an orange-red band with hexane/CH2Cl2/acetone (2:2:1 v:v:v) as eluant. Reduction in solvent volume in vacuo and addition of further hexane resulted in precipitation of the product as an orange-red solid: yield:1.71 g (32%). ¹H NMR (CDCl₃): δ 1.61 (br, 1H, CH₂), 2.25 (br, 1H, CH₂), 2.60 (br, 2H, CH₂), 4.64 (s, 5H, Cp), 7.22 - 7.71 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 92.3 (d, $J_{PP} = 38.9$ Hz, dppe), 66.9 (d, $J_{PP} = 38.9$ Hz, dppe). IR (CH₂Cl₂): ν (C=O) 1847 cm⁻¹. MALDI-MS (m/z): 624, $[M]^+$; 596 $[(M - CO)]^+$. Anal. Calcd (%) for C₃₂H₂₉OMoClP₂: C, 61.7; H, 4.7. Found: C, 61.6; H, 4.2.

Preparation of [MoCl(CO)(dppe)Cp]* (**1b**). Complex 1b was prepared by an identical procedure to that described for 1a from [MoCl(CO)₃Cp*] (2.88 g, 8.21 mmol) and dppe (4.57 g, 11.49 mmol) except that, after the initial addition of reagents, reflux was continued for 18 h. The product was obtained as an orange-red solid: yield 1.97 g (35%). ¹H NMR (CDCl₃): δ 1.33 (s, 15H, Cp*), 1.89 (br, 2H, CH₂), 2.18 (br, 1H, CH₂), 2.62 (br, 1H, CH₂), 7.00−7.62 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 88.2 (d, J_{PP} = 32.4 Hz, dppe), 65.2 (d, J_{PP} = 32.4 Hz, dppe). IR (CH₂Cl₂): ν(C≡O) 1822 cm⁻¹. MALDI-MS (*m*/*z*): 666 [(M − CO)]⁺. Anal. Calcd (%) for C₃₇H₃₉OMoClP₂: C, 64.2; H, 5.6. Found: C, 64.6; H, 5.3.

Preparation of [MoBr(CO)(dppe)Cp] (**2a**). Complex **2a** was prepared by an identical procedure to that described for **1a** from [MoBr-(CO)₃Cp] (0.50 g, 1.54 mmol) and dppe (0.92 g, 2.31 mmol). The product was obtained as an orange-red solid: yield 0.45 g (44%). ¹H NMR (CDCl₃): δ 1.55 (br, 1H, CH₂), 2.21 (br, 1H, CH₂), 2.56 (br, 2H, CH₂), 4.37 (s, 5H, Cp), 7.22 - 7.74 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 92.4 (d, J_{PP} = 38.9 Hz, dppe), 64.5 (d, J_{PP} = 38.9 Hz, dppe). IR (CH₂Cl₂): ν (C=O) 1849 cm⁻¹. MALDI-MS (*m/z*): 639 [(M -CO)]⁺. Anal. Calcd (%) for C₃₂H₂₉OMoBrP₂: C, 57.6; H, 4.4. Found: C, 57.3; H, 3.8.

Preparation of [*MoCl*(*CO*)(*PPh*₃)₂*Cp*] (**3a**). A mixture of [MoCl(CO)₃-Cp] (0.50 g, 1.79 mmol) and PPh₃ (2.34 g, 8.91 mmol) was dissolved in toluene (60 cm³), and the solution was refluxed for 18 h then evaporated to dryness. The residue, dissolved in CH₂Cl₂, was transferred to an *n*-hexanealumina chromatography column, and the product eluted as an orange-red band with hexane/CH₂Cl₂ (9:1 v:v) as eluant. Reduction of solvent volume *in vacuo* and addition of further hexane resulted in precipitation of the product as an orange-red solid: yield 0.801 g (60%). ¹H NMR (CDCl₃): δ 4.73 (t, SH, *J*_{HP} = 1.0 Hz, Cp), 7.12−7.63 (m, 36H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 57.5 (s, PPh₃). IR (CH₂Cl₂): ν(C≡O) 1792 cm⁻¹. MALDI-MS (*m*/*z*): 750, [M]⁺; 722 [(M − CO)]⁺; 715 [(M − Cl)]⁺; 488 [(M − PPh₃)]⁺; 460 [(M − CO − PPh₃)]⁺. Anal. Calcd (%) for C₄₂H₃₅OMoClP₂: *C*, 67.4; H, 4.7. Found: *C*, 67.2; H, 4.5.

*Preparation of [MoCl(CO)(PMe*₃)₂*Cp**] (**4b**). A mixture of [MoCl-(CO)₃Cp*] (0.50 g, 1.49 mmol) and PMe₃ (3.4 cm³ of a 1.0 M solution in toluene, 3.4 mmol) was dissolved in toluene (60 cm³), and the solution was refluxed for 18 h then evaporated to dryness. The residue, dissolved in CH₂Cl₂, was transferred to an *n*-hexane-alumina chromatography column, and the product eluted as an orange-red band with hexane/CH₂Cl₂ (9:1 v:v) as eluant. Recrystallization from pentane at −20 °C gave the product as an orange-red solid: yield 0.20 g (30%). ¹H NMR (CDCl₃): δ 1.32 (m, 18H, PMe₃), 1.72 (s, 15H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 18.1 (s, PMe₃). ES-MS (*m*/*z*): 448, [M]⁺. IR (CH₂Cl₂): ν(C=O) 1776 cm⁻¹. Anal. Calcd (%) for C₁₇H₃₃OMoClP₂: C, 45.7; H, 7.4. Found: C, 45.9; H, 7.9.

Preparation of [Mo(C=CPh)(CO)(dppe)Cp] (5a). A mixture of [MoCl(CO)(dppe)Cp] (0.50 g, 0.80 mmol) and HC≡CPh (0.50 g, 4.90 mmol) in methanol (100 cm^3) was refluxed for 1.5 h to give a green solution of [Mo(HC≡CPh)(dppe)Cp]Cl. Carbon monoxide gas was bubbled through the solution for 10 min to give an orange solution of the vinylidene [Mo(C=CHPh)(CO)(dppe)Cp]Cl $[\nu(CO) (CH_2Cl_2)$ 1902 $\rm cm^{-1}]$, which was treated with NaOMe (0.50 g, 9.3 mmol) to give a yellow solution, which was evaporated to dryness. The residue, dissolved in CH2Cl2, was transferred to a hexane-alumina column, and the product eluted as a yellow band with hexane/CH2Cl2/acetone (2:2:1 v:v:v) as eluant. Reduction in solvent volume in vacuo and addition of further hexane resulted in precipitation of the product as a yellow solid: yield 0.15 g (27%). ¹H NMR (CDCl₃): δ 1.77 (m, 1H, CH₂), 2.17 (m, 1H, CH₂), 2.42 (m, 2H, CH₂), 4.40 (s, 5H, Cp), 6.56 (d, 2H (AB), $J_{\text{HH}} \approx 8.0 \text{ Hz}$, C=CC₆H₅), 6.80 (m, 1H, C=CC₆H₅), 6.90 (m, 2H, C=CC₆H₅), 7.16–7.82 (m, 20H, Ph, dppe). ${}^{31}P{}^{1}H$ NMR (CDCl₃): δ 89.6 (d, *J*_{PP} = 39 Hz, dppe), 78.3 (d, *J*_{PP} = 39 Hz, dppe). IR (CH₂Cl₂): ν (C≡C) 2074 cm⁻¹, ν (C≡O) 1850 cm⁻¹. MALDI-MS (m/z): 663 $[(M - CO)]^+$. Anal. Calcd (%) for C₄₀H₃₄OMoP₂: C₁ 69.8; H, 4.9. Found: C, 69.1; H, 4.8.

Preparation of [Mo(C≡*CPh)(CO)(dppe)Cp*]* (*5b*). Complex 5b was prepared by an identical procedure to that described for 5a from [MoCl(CO)(dppe)Cp*] (0.50 g, 0.72 mmol), HC≡CPh (0.37 g, 3.61 mmol), and KOBu^t (0.40 g, 3.60 mmol). The product was isolated as a yellow solid: yield 0.12 g (22%). ¹H NMR: δ 1.42 (s, 15H, C₅Me₅), 1.86 (br, 2H, CH₂), 2.08 (br, 2H, CH₂), 6.38 (d, 2H (AB), *J*_{HH} ≈ 8 Hz, C₆H₅), 6.78 (m, 1H, C₆H₅), 6.89 (m, 2H, C₆H₅), 7.15−7.76 (m, 20H, Ph, dppe). ³¹P{¹H} NMR (CDCl₃): δ 86.10 (d, *J*_{PP} = 37 Hz, dppe), 77.2 (d, *J*_{PP} = 36 Hz, dppe). IR (CH₂Cl₂): ν(C≡C) 2065, ν(C≡O)

1828 cm⁻¹. ES-MS (*m*/*z*): 760, [M]⁺. Anal. Calcd (%) for C₄₅H₄₄OMoP₂: C, 71.2; H, 5.8. Found: C, 70.8; H, 6.3.

Preparation of [*Mo*(*C*≡*CC*₆*H*₄-4-*Me*)(*CO*)(*dppe*)*Cp*] (*6a*). Complex 6a was prepared by an identical procedure to that described for 5a from [MoCl(CO)(dppe)Cp] (0.50 g, 0.80 mmol), HC≡*CC*₆H₄-4-Me (0.56 g, 4.83 mmol), and NaOMe (0.50 g, 9.3 mmol). The product was isolated as a yellow solid: yield 0.11 g (20%). ¹H NMR: δ 1.78 (m, 1H, CH₂), 2.13 (s, 3H, C₆H₄-4-CH₃), 2.15 (br, 1H, CH₂), 2.36 (m, 2H, CH₂), 4.40 (s, 5H, Cp), 6.46 (d, 2H (AB), J_{HH} ≈ 8.0 Hz, C₆H₄-4-Me), 6.72 (d, 2H (AB), J_{HH} ≈ 8 Hz, C₆H₄-4-Me), 7.19−7.83 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 89.7 (d, J_{PP} = 39 Hz, dppe), 78.1 (d, J_{PP} = 39 Hz, dppe). IR (CH₂Cl₂): ν(C≡C) 2075, ν(C≡O) 1848 cm⁻¹. MAL-DI-MS (*m*/*z*): 676 [(M − CO)]⁺. HR ES+-MS (*m*/*z*): 704.1295 (C₄₁H₃₆OMoP₂ requires 704.1290).

Preparation of [*M*o(*C*≡*C*₆*H*₄-4-*M*e)(*CO*)(*dppe*)*Cp**] (*6b*). Complex **6b** was prepared by an identical procedure to that described for **5a** from [MoCl(CO)(dppe)Cp*] (0.25 g, 0.36 mmol), HC≡CC₆H₄-4-Me (0.25 g, 2.12 mmol), and KOBu^t (0.24 g, 2.12 mmol). The product was isolated as a yellow solid: yield 0.053 g (19%). ¹H NMR: δ 1.42 (s, 15H, C₅Me₅), 1.87 (br, 2H, CH₂), 2.10 (br, 2H, CH₂), 2.13 (s, 3H, C₆H₄-4-CH₃), 6.31 (d, 2H (AB), *J*_{HH} ≈ 8.0 Hz, C₆H₄-4-Me), 6.72 (d, 2H (AB), *J*_{HH} ≈ 8 Hz, C₆H₄-4-Me), 7.26-7.76 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 86.4 (d, *J*_{PP} = 36 Hz, dppe), 77.1 (d, *J*_{PP} = 36 Hz, dppe). IR (CH₂Cl₂): ν(C≡C) 2068, ν(C≡O) 1828 cm⁻¹. MALDI-MS (*m*/*z*): 746 [(M − CO)]⁺. Anal. Calcd (%) for C₄₆H₄₆OMoP₂: C, 71.5; H, 6.0. Found: C, 71.8; H, 5.6.

Preparation of [*Mo*(*C*≡*CPh*)(*CO*)₂(*PMe*₃)*Cp*] (**7a**). A mixture of [Mo(*C*≡*CPh*)(CO)₃Cp] (2.15 g, 6.22 mmol), PMe₃ (18.7 cm³ of a 1.0 M solution in toluene, 18.7 mmol), and Me₃NO · 2H₂O (1.38 g, 12.43 mmol) in NCMe (50 cm³) was stirred at room temperature for 0.5 h to give an orange-brown solution, which was evaporated to dryness. The residue, dissolved in CH₂Cl₂, was transferred to an *n*-hexane-alumina column, and the product eluted as a yellow band with hexane/CH₂Cl₂ (1:1 v:v) as eluant. Recrystallization from pentane at −20 °C gave the product as a yellow solid: yield 1.34 g (55%). ¹H NMR (CDCl₃): δ 1.55 (d, 9H, *J*_{HP} = 9.2 Hz, PMe₃), 5.26 (s, 5H, Cp), 7.01 (m, 1H, Ph_p), 7.15 (m, 4H), Ph_o and Ph_m. ³¹P{¹H} NMR (CDCl₃): δ 15.8 (s, PMe₃). IR (CH₂Cl₂): ν (C≡C) 2083, ν (C≡O) 1956, 1863 cm⁻¹. EI-MS (*m*/*z*): 396 [M]⁺, 368 [(M − CO)]⁺, 340 [(M − 2CO)]⁺, 322 [(M − PMe₃)]⁺. Anal. Calcd (%) for C₁₈H₁₉O₂MoP: C, 54.8; H, 4.8. Found: C, 54.6; H, 4.6.

Preparation of [*M*0(*C*≡*CPh*)(*CO*)₂(*PMe*₃)*Cp**] (**7b**). Complex 7b was prepared by an identical procedure to that described for 7a from [Mo(C≡CPh)(CO)₃Cp*] (2.60 g, 6.25 mmol), PMe₃ (18.8 cm³ of a 1.0 M solution in toluene, 18.8 mmol), and Me₃NO·2H₂O (1.39 g, 12.50 mmol). The product was isolated as a yellow solid: yield 1.78 g (62%). ¹H NMR (CDCl₃): δ 1.53 (d, 9H, *J*_{HP} = 9.2 Hz, PMe₃), 2.03 (s, 15H, Cp*), 7.12 (m, 1H, Ph_p), 7.24 (m, 2H), 7.31 (m, 2H), Ph_o and Ph_m. ³¹P{¹H} NMR (CDCl₃): δ 10.8 (s, PMe₃). IR (CH₂Cl₂): ν(C≡C) 2078, ν(C≡O) 1938, 1851 cm⁻¹. EI-MS (*m*/*z*): 466 [M]⁺, 438 [(M − CO)]⁺, 410 [(M − 2CO)]⁺, 390 [(M − PMe₃)]⁺, 390 [(M − 2CO − PMe₃)]⁺. HR ES+-MS (*m*/*z*): 466.0946 (C₂₃H₂₉O₂MoP requires 466.0954). Anal. Calcd (%) for C₂₃H₂₉O₂MoP: C, 59.5; H, 6.3. Found: C, 59.2; H, 5.8.

Preparation of $[Mo(C \equiv CPh)(CO)(PMe_3)_2Cp]$ (**8a**). A mixture of $[Mo(C \equiv CPh)(CO)_2(PMe_3)Cp]$ (1.34 g, 3.41 mmol) and PMe₃ (6.8 cm³ of a 1.0 M solution in toluene, 6.8 mmol) in toluene (80 cm³) was irradiated in a photochemical reactor (Hanovia, 125 W) for 3 h to give an orange-brown solution, which was evaporated to dryness. The residue, dissolved in *n*-hexane, was transferred to an *n*-hexane-alumina column, and two bands were eluted with hexane/ CH_2Cl_2 (4:1, v:v) as eluant. The first band was identified as the product **8a** by IR spectroscopy; the second band was identified by IR spectroscopy as starting material, **7a**. Complex **8a** was collected as the first band from the column and solvent removed. Recrystallization from pentane at

−20 °C gave the product as a yellow solid: yield 0.43 g (29%). ¹H NMR (CDCl₃): δ 1.51 (m, 18H, PMe₃), 4.92 (s, 5H, Cp), 6.96 (m, 1H, Ph_p), 7.06−7.19 (m, 4H, Ph_o and Ph_m). ³¹P{¹H} NMR (CDCl₃): δ 25.6 (s, PMe₃). IR (CH₂Cl₂): ν (C≡C) 2056, ν (C≡O) 1779 cm⁻¹. ES-MS (m/z): 444 [M]⁺, 416 [(M − CO)]⁺. Anal. Calcd (%) for C₂₀H₂₈OMoP₂: C, 54.3; H, 6.3. Found: C, 54.4; H, 6.5.

Preparation of [*M*o(*C*≡*CPh*)(*CO*)(*PMe*₃)₂*Cp*^{*}] (**8b**). Complex **8b** was prepared by an identical procedure to that described for **8a** starting from [Mo(*C*≡*CPh*)(*CO*)₂(*PMe*₃)*Cp*^{*}] (0.50 g, 1.07 mmol) and *PMe*₃ (2.2 cm³ of a 1.0 M solution in toluene, 2.2 mmol). The product was isolated as a yellow solid: yield 0.13 g (24%). ¹H NMR (CDCl₃): δ 1.42 (m, 18H, PMe₃), 1.89 (s, 15H, Cp^{*}), 6.98 (m, 1H, Ph_p), 7.10−7.22 (m, 4H, Ph_o and Ph_m). ³¹P{¹H} NMR (CDCl₃): δ 23.2 (s, PMe₃). IR (CH₂Cl₂): ν(C≡C) 2056, ν(C≡O) 1776 cm⁻¹. EI-MS (*m*/*z*): 514 [M]⁺, 410 [(M − CO − PMe₃)]⁺, 334 [(M − CO − 2PMe₃)]⁺. Anal. Calcd (%) for C₂₅H₃₈OMoP₂: C, 58.6; H, 7.4. Found: C, 58.6; H, 8.1.

Preparation of $[Mo(C \equiv CC_6H_4-4-Me)(CO)(PMe_3)_2Cp^*]$ (9b). Complex 9b was prepared by an identical procedure to that described for 8a starting from $[Mo(C \equiv CC_6H_4-4-Me)(CO)_2(PMe_3)Cp^*]$ (IR (CH₂Cl₂) ν (C=C) 2079, ν (C=O) 1936, 1849 cm⁻¹), which was obtained from the precursor [Mo(C≡CC₆H₄-4-Me)(CO)₃Cp*] $(IR (CH_2Cl_2) \nu(C \equiv C) 2094, \nu(C \equiv O) 2028, 1949, 1989(sh) cm^{-1})$ A mixture of $[Mo(C \equiv CC_6H_4-4-Me)(CO)_2(PMe_3)Cp^*]$ (1.50 g, 3.14 mmol) and PMe₃ (9.42 cm³ of a 1.0 M solution in toluene, 9.42 mmol) was irradiated in a photochemical reactor for 3 h to give an orange-brown solution, which was evaporated to dryness. The residue, dissolved in n-hexane, was transferred to an n-hexane-alumina column followed by elution with hexane/CH2Cl2 (4:1, v:v). The product was isolated as a yellow solid: yield 0.52 g (32%). ¹H NMR (CDCl₃): δ 1.37 (m, 18H, PMe₃), 1.81 (s, 15H, Cp*), 2.21 (s, 3H, C₆H₄-4-CH₃), 7.05 (d, 2H (AB), $J_{\rm HH} \approx 8.0 \,{\rm Hz}, \,{\rm C_6H_4-4-Me}$), 7.33 (d, 2H (AB), $J_{\rm HH} \approx 8 \,{\rm Hz}, \,{\rm C_6H_{4^-}}$ 4-Me). ³¹P{¹H} NMR (CDCl₃): δ 23.2 (s, PMe₃). IR (CH₂Cl₂): ν (C=C) 2057, ν (C=O) 1770 cm⁻¹. EI-MS (*m*/*z*): 528 [M]⁺. Anal. Calcd (%) for C₂₆H₄₀OMoP₂: C, 59.3; H, 7.6. Found: C, 59.4; H, 7.8.

Electronic Structure Calculations. All calculations were carried out using the Gaussian 03 package.³⁶ The model geometries for **5-H** and **8-H** were optimized using the B3LYP functional,³⁷ with no symmetry constraints. The Def2-SVP basis, obtained from the Turbomole library,³⁸ was used for all atoms. Frequency calculations were carried out on these optimized geometries at the corresponding levels and shown to have no imaginary frequencies. Molecular orbital computations were carried out on these optimized geometries, and the orbital contributions were generated with the aid of GaussSum.³⁹

Crystallography. The majority of details of the structure analyses carried out on complexes 5b, 6a, 6b, 7b, 8a, 8b, and 9b are given in Table 11. Single crystals of the complexes were obtained as follows: 5b, 6a/b, and 9b: vapor diffusion of *n*-pentane into a toluene solution of the complex to give yellow needles; 8a/b and 9b: solution of n-pentane at -20 °C; 7b: vapor diffusion of *n*-pentane into a CH₂Cl₂ solution of the complex to give yellow needles. X-ray data for all seven complexes were collected with an Oxford Diffraction X-Calibur 2 diffractometer equipped with an Oxford-Cryosystems low-temperature device at 100(2) K by means of Mo K α radiation and ω scans. Data were corrected for Lorenz and polarization factors, and absorption corrections were applied to all data. Structures were solved by direct methods with refinement by full-matrix least-squares based on F^2 against all reflections. Cell refinement and data reduction were carried out with CrysAlis CCD and CrysAlis RED software (Oxford Diffraction Ltd.). SHELXS-97⁴⁰ was employed for computing the structure solution and SHELXL-97⁴¹ for computing structure refinement. Difference Fourier syntheses were employed in positioning idealized H atoms, which were allowed to ride on their parent C atoms. All non-H atoms were refined anisotropically, and H atoms were included in calculated positions. C(10) and C(14)-C(18) of the Cp^{*} ring in structure 7b were

Tab	le 1	11.	Crystal	Data	and	Refinement	Parameters
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	5b	6a	6b	7b	8a	8b	9b
formula mass	C ₄₅ H ₄₄ MoOP ₂ 758.68	C ₄₁ H ₃₆ MoOP ₂ 702.58	С ₄₆ Н ₄₆ МоОР ₂ 772.71	C ₂₃ H ₂₉ MoO ₂ P 464.37	C ₂₀ H ₂₈ MoOP ₂ 442.30	C ₂₅ H ₃₈ MoOP ₂ 512.43	C ₂₆ H ₄₀ MoOP ₂ 526.46
λ (Å)	0.71069	0.71073	0.71069	0.71073	0.71073	0.71069	0.71069
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic
space group	P 21/n	P 21/c	P 21/c	P 21/c	Pbca	P-1	P-1
a (Å)	9.9199 (3)	12.3460(4)	17.151(5)	17.910(3)	14.749(4)	12.6102(4)	13.1792(4)
b (Å)	21.3484(7)	16.4490(5)	12.436(5)	8.1224(7)	8.9958(5)	13.4489(5)	13.6485(4)
c (Å)	17.4064(6)	16.0400(6)	18.564(5)	16.471(2)	31.027(2)	16.0881(5)	15.4833(4)
α (deg)	90	90	90	90	90	109.493(3)	73.776(3)
β (deg)	102.170(4)	97.2200(12)	108.536(5)	114.180(17)	90	100.261(3)	80.141(3)
γ (deg)	90	90	90	90	90	90.310(3)	82.039(3)
$V(\text{\AA}^3); Z$	3603.4(2); 4	3231.56(19); 4	3754(2); 4	2185.9(5); 4	4167(1); 8	2524.7(1); 4	2622.6(1); 4
absorp coeff (mm^{-1})	0.488	0.538	0.470	0.688	0.797	0.660	0.637
θ range (deg)	2.90-28.66	1.66-25.85	2.82-26.37	2.85 - 28.37	2.73-28.37	2.91-28.56	2.99-28.64
limiting indices (<i>h,k,l</i>)	-13, 12	0, 15	-21, 18	-22, 18	-18, 12	-15, 11	-17, 17
	-26, 28	0, 20	-13, 15	-10, 6	-11, 10	-17 , 17	-14, 18
	-23, 9	-19, 19	-23, 19	-18, 21	-27 , 41	-20 , 17	-19, 20
total reflns	8203	6130	7557	4839	4563	11 062	11 622
indep reflns, $I > 2\sigma(I)$	5313	3836	4750	3221	3396	6462	8662
R_1	0.0350	0.0782	0.0511	0.0450	0.0685	0.0301	0.0298
wR_2	0.0664	0.1862	0.0834	0.1178	0.1339	0.0524	0.0657
data completeness	88.4	98.1	98.3	88.6	88.9	86.1	86.3

disordered and therefore constrained and split into parts. Structures **8b** and **9b** contained two molecules in the asymmetric unit.

ASSOCIATED CONTENT

Supporting Information. Cyclic voltammograms of **6b** and **9b** showing $E_p(A)$ (irreversible), IR spectroelectrochemistry for $[5b]^{n+}$, $[6b]^{n+}$, and $[9b]^{n+}$, UV-visible spectroelectrochemistry for $[5b]^{n+}$, selected EPR spectra for $[3a]^+$, $[4b]^+$, $[8b]^+$, $[1a]^+$, $[1b]^+$, $[6a]^+$, and $[6b]^+$, and CIF files giving crystallographic data for complexes **5b**, **6a**, **6b**, **7b**, **8a**, **8b**, and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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