

Spectroscopic Properties and Electronic Structure of the Cycloheptatrienyl Molybdenum Alkynyl Complexes $[Mo(C \equiv CR)(Ph_2PCH_2CH_2PPh_2)(\eta-C_7H_7)]^{n+}$ (n = 0 or 1; $R = Bu^t$, Fc, CO₂Me, or C₆H₄-4-X, $X = NH_2$, OMe, Me, H, CHO, CO₂Me)

Neil J. Brown,[†] David Collison,^{*,‡} Ruth Edge,[‡] Emma C. Fitzgerald,[§] Madeleine Helliwell,[§] Judith A. K. Howard,[†] Hannah N. Lancashire,[§] Paul J. Low,^{*,†} Joseph J. W. McDouall,^{*,§} James Raftery,[§] Charlene A. Smith,[§] Dmitry S. Yufit,[†] and Mark W. Whiteley^{*,§}

[†]Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, U.K., [‡]EPSRC National Service for EPR Spectroscopy, School of Chemistry, University of Manchester, Manchester, M13 9PL, U.K., and [§]School of Chemistry, University of Manchester, Manchester, M13 9PL, U.K.

Received December 16, 2009

A series of molybdenum alkynyl complexes $[Mo(C=CR)(dppe)(\eta-C_7H_7)]$ featuring a range of alkynyl substituents R with varying electron-donating and -withdrawing properties have been prepared. Oxidation of representative members of the series to the corresponding 17-electron radical cations has been achieved through both chemical oxidation and *in situ* spectroelectrochemical methods. The largely metal-centered character of the HOMO in this class of compounds has been established through a combination of experimental measurements (IR, UV-vis-NIR, EPR spectroscopies) and DFT-based calculations and rationalized in terms of the stabilization of the metal d_{xy} , d_{yz} , d_{xz} , and $d_{x^{2}-y^{2}}$ through π - and δ -interactions with the C_7H_7 ring and concomitant destabilization of the $d_{z^{2}}$ orbital.

Introduction

Metal alkynyl complexes have been the focus of intense research activity for many decades.^{1,2} Much of the early work on synthetic methodology and structural properties of alkynyl complexes has developed into current studies of alkynyl complexes as molecular materials with potential

(4) (a) Lapinte, C. J. Organomet. Chem. 2008, 693, 793. (b) Paul, F.; Lapinte, C. In Unusual Structures and Physical Properties in Organometallic Chemistry; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; John Wiley and Sons Ltd.: New York, 2002. applications in electronic,³ magnetic,⁴ and optical⁵ devices. Central to these investigations is an understanding of electronic structure and consequently the degree of electronic interaction between the metal center and the alkynyl ligand;⁶ recent work on the group 8 metal systems $[M(C \equiv CR)-(dppe)Cp^*]^{n+}$ (M = Fe⁷⁻¹⁰ or Ru;^{11,12} Cp* = C₅Me₅; n = 0 or 1) demonstrates a strong dependence on the identity of the metal. Thus the iron (3d) complexes exhibit substantial metal character in the frontier orbitals, whereas the HOMOs of the ruthenium (4d) analogues show more alkynyl ligand character, leading to interest in heterometallic systems containing these moieties.¹³

The cycloheptatrienyl molybdenum auxiliary Mo(dppe)-(η -C₇H₇) is well recognized as an isoelectronic analogue of the widely explored group 8 systems M(dppe)Cp* (M = Fe

^{*}Corresponding authors. E-mail: p.j.low@durham.ac.uk; Mark. Whiteley@manchester.ac.uk.

⁽¹⁾ Nast, R. Coord. Chem. Rev. 1982, 47, 89.

⁽²⁾ Long, N. J.; Williams, C. K. Angew. Chem., Int. Ed. 2003, 42, 2586.
(3) (a) Gauthier, N.; Argouarch, G.; Paul, F.; Humphrey, M. G.; Toupet, L.; Ababou-Girad, S.; Sabbah, H.; Hapiot, P.; Fabre, B. Adv. Mater. 2008, 20, 1952. (b) Low, P. J. Dalton Trans. 2005, 2821. (c) Kim, B.; Beebe, J. M.; Olivier, C.; Rigaut, S.; Touchard, D.; Kushmerick, J. G.; Zhu, X. Y.; Frisbie, C. D. J. Phys. Chem. C 2007, 111, 7521.

^{(5) (}a) Samoc, M.; Dalton, G. T.; Gladysz, J. A.; Zheng, Q.; Velkov, Y.; Ågren, H.; Norman, P.; Humphrey, M. G. *Inorg. Chem.* **2008**, *47*, 9946. (b) Samoc, M.; Gauthier, N.; Cifuentes, M. P.; Paul, F.; Lapinte, C.; Humphrey, M. G.; Dalton, G. T. *Angew. Chem., Int. Ed.* **2008**, *47*, 629. (c) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291. (d) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349. (e) Morrall, J. P.; Dalton, G. T.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **2008**, *55*, 61. (f) Powell, C. E.; Humphrey, M. G. *Coord. Chem. Rev.* **2004**, *248*, 725.

^{(6) (}a) Koentjoro, O. F.; Rousseau, R.; Low, P. J. Organometallics
2001, 20, 4502. (b) Lichtenberger, D. L.; Gruhn, N. E.; Renshaw, S. K. J. Mol. Struct. 1997, 405, 79. (c) Lichtenberger, D. L.; Renshaw, S. K.; Wong, A.; Tagge, C. D. Organometallics 1993, 12, 3522. (d) Delfs, C. D.; Stranger, R.; Humphrey, M. G.; McDonagh, A. M. J. Organomet. Chem. 2000, 607, 208. (e) McGrady, J. E.; Lovell, T.; Stranger, R.; Humphrey, M. G. Organometallics 1997, 16, 4004.

⁽⁷⁾ Connelly, N. G.; Gamasa, M. P.; Gimeno, G.; Lapinte, C.; Lastra, E.; Maher, J. P.; Le Narvor, N.; Rieger, A. L.; Rieger, P. H. J. Chem. Soc., Dalton Trans. **1993**, 2575.

⁽⁸⁾ Denis, R.; Toupet, L.; Paul, F.; Lapinte, C. Organometallics 2000, 19, 4240.

⁽⁹⁾ Costuas, K.; Paul, F.; Toupet, L.; Halet, J.-F; Lapinte, C. Organometallics 2004, 23, 2053.

⁽¹⁰⁾ Paul, F.; Toupet, L.; Thépot, J.-Y.; Costuas, K.; Halet, J.-F.; Lapinte, C. Organometallics **2005**, *24*, 5464.

⁽¹¹⁾ Paul, F.; Ellis, B. G.; Bruce, M. I.; Toupet, L.; Roisnel, T.; Costuas, K.; Halet, J.-F.; Lapinte, C. *Organometallics* **2006**, *25*, 649.

⁽¹²⁾ Fox, M. A.; Roberts, R. L.; Khairul, W. M.; Hartl, F.; Low, P. J. J. Organomet. Chem. 2007, 692, 3277.

^{(13) (}a) Gauthier, N.; Oliver, C.; Rigaut, S.; Touchard, D.; Roisnel, T.; Humphrey, M. G.; Paul, F. Organometallics 2008, 27, 1063. (b) Bruce, M. I.; Costuas, K.; Davin, T.; Ellis, B. G.; Halet, J.-F.; Lapinte, C.; Low, P. J.; Smith, M. E.; Skelton, B. W.; Toupet, L.; White, A. H. Organometallics 2005, 44, 3261. (c) Szafert, S.; Paul, F.; Meyer, W. E.; Gladysz, J. A.; Lapinte, C. C. R. Chem. 2008, 11, 693.

or Ru) and has an extensive organometallic chemistry as a supporting group to alkynyl-based ligands;14-17 indeed alkynyl derivatives of the type $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]^{n+1}$ $(R = Ph \text{ or } Bu^{t}; n = 0 \text{ or } 1)$ have been in the vanguard of spectroscopic¹⁴ and structural investigations¹⁸ on the redox chemistry of metal alkynyl complexes. Although formally isoelectronic with $M(dppe)Cp^*$ (M = Fe, Ru), the Mo(dppe)- $(\eta$ -C₇H₇) auxiliary is distinctive in the combination of a 4d metal system with very low formal potentials for one-electron oxidation¹⁹ exemplified by a comparison of the alkynyl derivatives {cf. $E_{1/2}$ (V vs SCE, CH₂Cl₂/0.2 M [NBu₄]BF₄), $[M(C \equiv CPh)(dppe)(\eta-L)], M = Ru, L = Cp^*, 0.35;^{20} M = Fe, L = Cp^*, -0.04;^{20} M = Mo, L = \eta-C_7H_7, -0.15^{14}\}.$ The $Mo(dppe)(\eta-C_7H_7)$ auxiliary in combination with the alkynyl fragment, which might be considered as the prototypical unsaturated carbon-based ligand,²¹ therefore offers an interesting system for further exploration of the M-C=C interaction. In this work a series of alkynyl complexes [Mo(C=CR)(dppe)- $(\eta - C_7 H_7)$]ⁿ⁺ (n = 0 or 1; R = Bu^t, Fc, CO₂Me, C₆H₄-4-X; $X = NH_2$, OMe, Me, H, CHO, CO₂Me) have been studied using a range of spectroscopic, including spectroelectrochemical, and theoretical techniques. Together these investigations demonstrate that the complexes [Mo(C=CR)- $(dppe)(\eta-C_7H_7)^{n+}$ feature largely metal-localized occupied frontier orbitals.

Results and Discussion

Synthetic Studies. An overview of the synthetic work is given in Scheme 1. The key advances are (i) the development of an improved synthetic route to the previously reported derivatives [Mo(C=CR)(dppe)(η -C₇H₇)] [R = Ph, 2a;¹⁴ Bu^t, 2b;¹⁴ Fc, 2c²² {Fc = ferrocenyl}] starting from [MoBr-(dppe)(η -C₇H₇)] (1) and (ii) the synthesis of a new series of aryl-alkynyl complexes [Mo(C=CC₆H₄-4-X)(dppe)-(η -C₇H₇)]^{0/+1} featuring a range of X groups with varying donor/acceptor properties [X = NH₂, 2e; OMe, 2f; Me, 2g; CHO, 2h; CO₂Me, 2i]. The non-aryl alkynyl series (2b,c) was also extended with the preparation of the methyl propiolate derivative [Mo(C=CCO₂Me)(dppe)(η -C₇H₇)], 2d. In previous studies,¹⁴ alkynyl complexes [Mo(C=CR)-

In previous studies,¹⁴ alkynyl complexes [Mo(C=CR)-(dppe)(η -C₇H₇)] were obtained by deprotonation of the corresponding vinylidenes [Mo{C=C(H)R}(dppe)(η -C₇H₇)]PF₆, prepared in turn from the sandwich system [Mo(η -C₆H₅Me)-(η -C₇H₇)]PF₆ through sequential reaction with dppe and the terminal alkyne HC=CR. However, we have recently

(17) Grime, R. W.; Helliwell, M.; Hussain, Z. I.; Lancashire, H. N.; Mason, C. R.; McDouall, J. J. W.; Mydlowski, C. M.; Whiteley, M. W. *Organometallics* **2008**, *27*, 857.

(18) (a) Beddoes, R. L.; Bitcon, C.; Ricalton, A.; Whiteley, M. W. J.
 Organomet. Chem. 1989, 367, C21. (b) Beddoes, R. L.; Bitcon, C.; Whiteley,
 M. W. J. Organomet. Chem. 1991, 402, 85.

(19) (a) Petrovic, D.; Hrib, C. G.; Randoll, S.; Jones, P. G.; Tamm, M. Organometallics **2008**, *27*, 778. (b) Tamm, M.; Bannenberg, T.; Dressel,

Scheme 1. Routes to $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]$ Complexes



described a convenient route to $[MoBr(dppe)(\eta-C_7H_7)]$ (1),¹⁷ which permits the ready syntheses of an extended range of alkynyl derivatives. Thus, reaction of 1 with HC=CR in refluxing methanol gives the vinylidene complexes $[Mo-{C=C(H)R}(dppe)(\eta-C_7H_7)]^+$ directly as the bromide salts, which were not isolated but deprotonated *in situ* by base (KOBu^t or NaOMe), resulting in precipitation of the alkynyl complexes $[Mo(C=CR)(dppe)(\eta-C_7H_7)]$. Alternatively, fluoride-mediated desilylation/metalation approaches²³ have also been employed in certain cases. For example, reaction of Me₃SiC=CC₆H₄-4-OMe with $[MoBr(dppe)(\eta-C_7H_7)]$ and KF in methanol afforded **2f**, in yields comparable to those obtained from the terminal alkyne. The new aryl-alkynyl complexes **2e**-**2i** were isolated as blue-black, brown, or green solids, in yields in the range ca. 30–60%.

The previously reported 17-electron radical cations [Mo- $(C \equiv CR)(dppe)(\eta - C_7H_7)$][BF₄] (R = Ph, [2a]⁺; R = Bu^t, [2b]⁺)¹⁴ were also prepared by respective oxidation of 2a or 2b with [FcH][BF₄] in CH₂Cl₂ and obtained as deep purpleblue ([2a]⁺) or orange ([2b]⁺) solids. These isolated examples of the radical cations facilitate structural and other investigations, complemented by studies of the radicals generated *in situ* by spectroelectrochemical techniques.

Spectroscopic Studies. The complexes 2a-2i were characterized by microanalysis, mass spectrometry, infrared spectroscopy, and by ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectroscopies (see Experimental Section and Table 1). The electronic properties of the aryl substituent X in $[Mo(C \equiv CC_6H_4-4-$ X)(dppe)(η -C₇H₇)] correlate with trends in ν (C=C) data in the infrared spectra and δC_{α} in the ¹³C{¹H} NMR data. Thus in progressing from electron-releasing to electronwithdrawing substituents X in the series 2e-2i, $\nu(C=C)$ decreases from 2055 cm^{-1} (2e) to 2030, 1993(shoulder) cm^{-1} (2i). In the case of the methyl propiolate complex 2d, the combination of a strongly electron-donating metal system and a highly electron-withdrawing alkynyl substituent results in an exceptionally low value for ν (C=C) (2020 cm $^{-1}).$ In the ^{13}C NMR spectra the C_{α} resonances were readily identified by the characteristic J_{CP} coupling (ca. 26) Hz), the chemical shift of which tracked the electronic properties of the alkynyl substitutent. Thus, in the case of

⁽¹⁴⁾ Adams, J. S.; Bitcon, C.; Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. J. Chem. Soc., Dalton Trans. 1987, 3049.

⁽¹⁵⁾ Beddoes, R. L.; Bitcon, C.; Grime, R. W.; Ricalton, A.; Whiteley, M. W. J. Chem. Soc., Dalton Trans. **1995**, 2873.

^{(16) (}a) Cambridge, J.; Choudhary, A.; Friend, J.; Garg, R.; Hill, G.; Hussain, Z. I.; Lovett, S. M.; Whiteley, M. W. J. Organomet. Chem. **1999**, 577, 249. (b) Lancashire, H. N.; Ahmed, R.; Hague, T. L.; Helliwell, M.; Hopgood, G. A.; Sharp, L.; Whiteley, M. W. J. Organomet. Chem. **2006**, *691*, 3617.

^{B.; Fröhlich, R.; Holst, C.} *Inorg. Chem.* 2002, *41*, 47.
(20) Bitcon, C.; Whiteley, M. W. J. Organomet. Chem. 1987, 336, 385.

⁽²⁰⁾ Bricon, C., Whiteley, W. W. J. Organomet. Chem. **198**7, 550, 385 (21) Bruce, M. I.; Low, P. J. Adv. Organomet. Chem. **2004**, 50, 179.

 ⁽²²⁾ Hussain, Z. I.; Whiteley, M. W.; McInnes, E. J. L. J. Organomet. Chem. 1997, 543, 237.

⁽²³⁾ Bruce, M. I.; Hall, B. C.; Kelly, B. D.; Low, P. J.; Skelton, B. W.; White, A. H. J. Chem. Soc., Dalton Trans. **1999**, 3719.

1263

			Table 1. ¹³ 0	C{ ¹ H} NMR Data f	for [Mo(C≡CR)(dp	$pe)(\eta$ - $C_7H_7)]$			
	$2a^a$	$2\mathbf{b}^{a}$	$2c^{a}$	$2d^{a}$	$2e^{b}$	$2\mathbf{f}^{b}$	$\mathbf{2g}^{a}$	$2\mathbf{h}^{b}$	$2\mathbf{i}^b$
Cα	t, 141.4 $J_{\rm CP} = 26$	t, 113.1, $I_{} = 27$	t, 132.0, $I_{} = 27$	t, 157.7, $I_{} = 24$	not observed	not observed	t, 139.3, $I_{} = 26$	t, 160.0, $I_{} = 26$	not observed
C_{eta}	br, 121.6	br, 132.6	br, 116.2	br, 115.0	br, 119.6	br, 120.9	$f_{1}^{CP} = 20$ t, 126.0, $I_{20} = 2$	$_{1,132.9}^{\text{JCP}} = 20$ t, 132.9, $I_{20} = 8$	t, 130.9, $I_{CD} = 5$
C_7H_7	s, 86.8	s, 86.6	s, 86.8	s, 87.8	s, 87.0	s, 87.0	s, 87.2	s, 87.3	s, 87.2
$CH_2 \times 2$ C1	m, 26.3 s. 122.6	m, 26.7	m, 26.6	m, 26.7	m, 26.6 s. 121.3	m, 26.5 s. 121.8	m, 26.8 s. 121.8	m, 26.5 s. 130.8	m, 26.5 s. 132.8
C2	s, 129.3				s, 130.1	s, 130.0	s, 129.0	s, 134.2	s, 128.7
C3	s, 128.1				s, 114.3	s, 112.9	s, 128.2	s, 128.7	s, 128.7
C4	s 128.6				s, 142.7	s, 155.9	s, 132.6	s, 124.8	s, 123.5
Ph_i	m, 135.7, 140.8	m, 136.3, 141.7	m, 135.9, 141.2	m, 135.6, 140.2	m, 136.3, 141.2	m, 136.2, 141.1	m, 136.3, 141.3	m, 135.3, 140.6	m, 135.5, 140.6
Ph_o	m, 131.4, 133.8	dd, 131.2, 134.4,	dd, 134.4, 134.4,	dd, 132.2, 133.8,	dd, 131.8, 134.1,	dd, 131.7, 134.0,	dd, 131.9, 134.2,	dd, 131.6, 133.9,	dd, 131.6, 133.9,
		$J_{\rm CP} = 6, 5$	$J_{\rm CP}=5,5$	$J_{ m CP}=5,5$	$J_{\rm CP} = 5, 6$	$J_{\rm CP} = 5, 6$	$J_{ m CP}=5,5$	$J_{\rm CP}=6,6$	$J_{\rm CP} = 5, 6$
Ph_{m}	m, 127.7, 128.0	dd, 127.4, 127.9,	dd, 127.6, 128.0,	br 128.2, 128.6	dd, 127.9, 128.3,	dd, 127.9, 128.3,	dd, 128.1, 128.5,	dd, 128.2, 128.4,	dd, 128.1, 128.4,
Dh	9 801 1 201 9	$J_{\rm CP} = 4, 5$	$J_{\rm CP} = 4, 5$	8 0CL 7 0CL 3	$J_{\rm CP} = 5, 4$	$J_{\rm CP} = 5, 4$	$J_{\rm CP} = 7, 4$	$J_{\rm CP} = 5, 4$	$J_{\rm CP} = 5, 4$
substituent	0, 14 1.1, 140.0	s, 28.3, CMe ₃	s, 68.5, C ₅ H ₅	s, 50.9, OCH ₃	o, 140-7, 147-1	s, 55.2, OMe	s, 21.1, CH ₃	s, 190.7, C=O	s, 51.7, OCH ₃
substituent		s, 31.4, C(CH ₃)	s, 74.5, C _{ipso} s, 68.1, C _A , s, 65.8, C _B ^b	s, 152.3, C=0					s, 167.1, C=0

^{*a*} 100 MHz spectra; s = singlet, d = doublet, t = triplet, multiplet, br = broad; chemical shifts downfield from SiMe₄, coupling constants in Hz. In CD₂Cl₂ solution with a trace of CoCp₂. All spectra recorded at ambient temperature. All assignments for the aryl rings were made in comparison to the free ligand. Diagram showing the atom-labeling schemes used in the summary of NMR data.



^b125 MHz spectra.



Figure 1. Plot of the molecular structure of **2b** showing the atom-labeling scheme. In this and all subsequent structural figures, thermal ellipsoids are plotted at 50% probability unless stated otherwise. Hydrogen atoms have been omitted for clarity.



Figure 2. Plot of the molecular structure of 2d showing the atom-labeling scheme.

the phenyl and tolyl alkynyl complexes **2a** and **2g**, C_{α} was observed near 140 ppm (Table 1). The introduction of the more electron-withdrawing groups (e.g., **2d**, **2h**) results in significant shift of the C_{α} resonance to nearer 160 ppm (Table 1), while in the case of the electron-donating alkyl derivative **2b**, C_{α} was observed at 113 ppm. Finally the ³¹P{¹H} NMR resonances for **2a**-**2i** all fall within a very narrow range (δ 64-66 ppm) with little dependence upon the identity of the alkynyl substituent. Similar trends are apparent in equivalent ³¹P{¹H} NMR data reported for [M(C= $CC_{6}H_{4}$ -4-X)(dppe)Cp*] (M = Fe, δ 100-102 ppm;⁸ M = Ru, δ 81-82.5 ppm¹¹).

Structural Investigations. The X-ray crystal structures of **2b**, **2d**, **2g**, **2h**, and **2i** and the 17-electron radical [**2b**][BF₄] have been determined (Figures 1 to 6, respectively), and important bond lengths and angles (including those for the previously reported structures of **2a** and [**2a** $]^+$)^{18b} are summarized in Table 2. In the 18-electron systems, the key



Figure 3. Plot of the molecular structure of 2g showing the atom-labeling scheme.



Figure 4. Plot of the molecular structure of 2h showing the atom-labeling scheme.

Mo- C_{α} distance exhibits a small dependence on the identity of the alkynyl substituent and decreases from around 2.14 Å in **2a**, **2b**, **2d**, and **2g** to 2.11–2.12 Å in **2h** and **2i**, which feature electron-withdrawing aryl-alkynyl substituents. The Mo-P bond length is a sensitive probe of metal electron density through M-P back-bonding effects,²⁴ and the slight elongation of the Mo-P distances in **2a**, **2d**, **2h**, and **2i** by comparison with **2b** and **2g** is consistent with the electronic parameters of the alkynyl substituents. Finally the longer C_{β} - $C_{(substituent)}$ bond length [C(9)–C(10)] in **2b** probably reflects the different hybridization at C(10) of the alkyl substituent.

The X-ray structures of the redox pairs $2a/[2a]^+$ and $2b/[2b]^+$ permit an examination of the structural effects of one-electron oxidation within this series. The principal structural modifications in each redox pair resulting from removal of an electron are remarkably consistent and comprise

^{(24) (}a) Cordiner, R. L.; Albesa-Jové, D.; Roberts, R. L.; Farmer, J. D.; Puschmann, H.; Corcoran, D.; Goeta, A. E.; Howard, J. A. K.; Low, P. J. J. Organomet. Chem. **2005**, 690, 4908. (b) Manna, J.; John, K. D.; Hopkins, M. D. Adv. Organomet. Chem. **1995**, 38, 79.



Figure 5. Plot of the molecular structure of 2i showing the atom-labeling scheme.



Figure 6. Plot of the structure of $2b[BF_4]$ (as one of four crystallographically independent ion pairs in the asymmetric unit) showing the atom-labeling scheme. Thermal ellipsoids are plotted at 20% probability.

a contraction in the Mo– C_{α} bond length (0.07 Å for both cases) and an increase in the Mo–P bond length (0.06 Å for **2a**/[**2a**]⁺, 0.07 Å for **2b**/[**2b**]⁺); the latter change is readily accounted for by Mo–P back-bonding effects, while the contraction in the Mo– C_{α} distance, although probably largely electrostatic in origin, is further rationalized by a DFT treatment (see below).

Electrochemistry. A key objective of this investigation is to explore the redox chemistry of the metal alkynyls [Mo- $(C \equiv CR)(dppe)(\eta - C_7H_7)$] to facilitate comparison with [M- $(C \equiv CR)(dppe)Cp^*$] (M = Fe or Ru) analogues. To commence these investigations, we examined the cyclic voltammetry of each of the complexes 2a-2i at a platinum electrode in CH₂Cl₂ (Table 3).

Under these conditions each of the complexes 2a-2i undergoes a diffusion-controlled, chemically reversible,

one-electron oxidation with the separation between cathodic and anodic peak potentials comparable to that determined for the internal ferrocene standard. The anisole derivative 2f also exhibits a second oxidation at a significantly more positive potential, which is only partially chemically reversible and likely due to oxidation of the anisole moiety. Oneelectron oxidation of the methyl propiolate derivative 2d is relatively unfavorable (in the thermodynamic sense) and reflects the electron-withdrawing properties of the ester group bonded directly to the alkynyl moiety. For comparison, Table 3 also presents electrochemical data for oneelectron oxidation of the analogous group 8 complexes $[M(C \equiv CC_6H_4-4-X)(dppe)Cp^*]$ (M = Fe, 3a, 3e, 3f, 3g; Ru, 4a, 4e, 4f, 4g). One-electron oxidation of the various members of the molybdenum series 2e-2i is clearly more thermodynamically favorable than for analogous group 8 complexes. However the $E_{1/2}$ values of the molybdenum arylalkynyl complexes 2a and 2e-2i span a range of only ca. 160 mV and are therefore less sensitive to the identity of the alkynyl substituent than the analogous ruthenium complexes, for which the equivalent range is in excess of 300 mV.

IR Spectroelectrochemical Analysis. Spectroelectrochemical methods permit the convenient and rapid collection of spectroscopic data from each member of a redox-related family of compounds.²⁵ In the case of metal alkynyl complexes, the characteristic $\nu(C \equiv C)$ 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,^{8,11,12,26} especially when coupled with observation of other IR-active bands elsewhere in the molecule.²⁷

Given that π -back-bonding effects make a minimal contribution to net M-C bond strength in d⁶ pseudo-octahedral alkynyl complexes,^{11,12} the magnitude of the negative shift in ν (C=C) resultant upon one-electron oxidation appears to be a good first-order indicator of the extent of the character of the redox-active frontier orbital within a series of similar complexes. Thus the large negative shifts of $\nu(C=C)$ observed upon oxidation of $[Ru(C \equiv CR)(dppe)Cp^*]$ (-90) to -145 cm^{-1}) are consistent with depopulation of an orbital with a large amount of C=C bonding character and significant radical-ligand character in the cations $[Ru(C \equiv CR)(dppe)Cp^*]^{+,11,12}$ By contrast the Fe complexes [Fe-(C=CR)(dppe)Cp*] feature more metal-centered oxidation processes, with less alkynyl ligand character in the resulting semioccupied orbital, and consequently much smaller shifts in ν (C=C), upon oxidation (ca. 0 to -70 cm^{-1}).^{8,9} Several factors may contribute to the marked differences between the Fe and Ru series, but key considerations appear to be the larger spatial extension (and better polarizability) of 4d

 ^{(25) (}a) Krejeik, M.; Danek, M.; Hartl, F. J. Electroanal. Chem. 1991, 317, 179. (b) Spectroelectrochemistry; Kaim, W., Klein, A., Eds.; Royal Society of Chemistry: Cambridge, 2008.

^{(26) (}a) Bruce, M. I.; Low, P. J.; Hartl, F.; Humphrey, P. A.; de Montigny, F.; Jevric, M.; Lapinte, C.; Perkins, G. J.; Roberts, R. L.; Skelton, B. W.; White, A. H. *Organometallics* **2005**, *24*, 5241. (b) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. J. Am. Chem. Soc. **2000**, *122*, 1949.

^{(27) (}a) Fox, M. A.; LeGuennic, B.; Roberts, R. L.; Baines, T. E.; Yufit, D. S.; Albesa-Jové, D.; Halet, J.-F.; Hartl, F.; Howard, J. A. K.; Low, P. J. J. Am. Chem. Soc. **2008**, 130, 3566. (b) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. J. Am. Chem. Soc. **1997**, 119, 775.

Table 2. Selected Bond Length and Bond Angle Data for the Alkynyl Complexes $[Mo(C_{\alpha} \equiv C_{\beta}R)(dppe)(\eta - C_{7}H_{7})]^{n+}$ (n = 0 or 1)

	2a	2b	2d	2g	2h	2i	[2a] ⁺	[2 b] ⁺
			Bond Le	engths (Å)				
$\begin{array}{l} Mo-C_{\alpha}\\ C_{\alpha}-C_{\beta}\\ C_{\beta}-C_{(substituent)}\\ Mo-P \end{array}$	2.138(5) 1.205(6) 1.434(7) 2.477(1), 2.467(1)	2.1382(17) 1.216(2) 1.485(2) 2.4648(4), 2.4520(4)	2.146(2) 1.179(3) 1.436(3) 2.4731(6), 2.4686(6)	2.140(5) 1.196(6) 1.441(7) 2.4677(14), 2.4525(14)	2.1094(19) 1.212(3) 1.426(3) 2.4767(5), 2.4772(5)	2.122(7) 1.191(10) 1.453(10) 2.477(2), 2.455(2)	2.067(9) 1.196(11) 1.445(12) 2.538(2), 2.528(3)	2.070(11) 1.201(12) 1.507(14) 2.537(3), 2.528(3)
			Bond An	ngles (deg)				
$Mo-C_{\alpha}-C_{\beta}$ $C_{\alpha}-C_{\beta}-C_{(substituent)}$ $P-Mo-P$ $P-Mo-C_{\alpha}$	178.5(4) 177.9(5) 78.2(1) 83.8(2), 77.3(2)	175.17(14) 177.42(18) 78.312(14) 80.24(4), 78.67(4)	176.33(18) 177.6(2) 78.38(2) 80.52(5), 79.18(5)	174.0(5) 174.6(6) 78.39(5) 81.59(13), 77.96(13)	178.54(16) 176.71(19) 78.558(18) 84.47(5), 76.73(5)	174.17(6) 171.0(8) 78.63(7) 81.21(2), 77.43(2)	174.6(8) 175.0(10) 78.4(1) 83.5(3), 75.1(3)	175.1(10) 178.2(12) 78.70(10) 80.5(3), 75.0(3)

Table 3. Cyclic Voltammetric Data for $[M(C \equiv CR)(dppe)(\eta-L)]$ (M = Mo, L = C₇H₇; M = Fe, Ru, L = Cp*)^h

compound	$E_{1/2}$ (V)	notes
2a (-30 °C)	-0.72	а
2b (-30 °C)	-0.82	а
2c	-0.79, +0.07	b
2d (-30 °C)	-0.50	а
2e	-0.81	a,f
2f (-30 °C)	-0.74, +0.60	a,f,g
2g (-30 °C)	-0.72	а
2h	-0.70	а
2i	-0.65	а
3a , $[Fe(C \equiv CC_6H_5)(dppe)Cp^*]$	-0.61	С
3e , $[Fe(C \equiv CC_6H_4-4-NH_2)(dppe)Cp^*]$	-0.71	С
3f , $[Fe(C \equiv CC_6H_4-4-OMe)(dppe)Cp^*]$	-0.67	С
3g, [Fe(C=CC ₆ H ₄ -4-Me)(dppe)Cp*]	-0.64	С
4a, $[Ru(C \equiv CC_6H_5)(dppe)Cp^*]$	-0.16	d
4e, $[Ru(C \equiv CC_6H_4 - 4 - NH_2)(dppe)Cp^*]$	-0.41	е
4f , $[Ru(C \equiv CC_6H_4-4-OMe)(dppe)Cp^*]$	-0.31	е
4g, $[Ru(C \equiv CC_6H_4-4-Me)(dppe)Cp^*]$	-0.15	d

^{*a*} This work. ^{*b*} Ref 22. ^{*c*} Ref 8. ^{*d*} Ref 12. ^{*e*} Ref 11. ^{*f*} 0.1 M NBu₄PF₆/THF (FcH/FcH⁺ = 0.00 V). ^{*g*} Irreversible oxidation at +0.60 V. ^{*h*} All potentials are reported vs FcH/FcH⁺ (FcH/FcH⁺ = 0.00 V) from 0.1 M NBu₄PF₆/CH₂Cl₂ solutions at ambient temperature unless stated otherwise. Data for **2c** originally reported vs SCE in 0.2 M NBu₄BF₄ (FcH/FcH⁺ = 0.56 V)²² have been adjusted to the FcH/FcH⁺ reference scale adopted in the current work.

versus 3d metal orbitals and the energies of these metal orbitals relative to the alkynyl π -system.

Guided by the results of the cyclic voltammetry, an IR spectroelectrochemical investigation was carried on each of the molybdenum complexes 2a-2i. In each case, the stability of the radical cation (and hence the validity of the $\nu(C \equiv C)$ data) was established by back-reduction, which resulted in full recovery of the IR spectrum assigned to the 18-electron precursor. Table 4 summarizes the data obtained and the shifts in $\nu(C \equiv C)$ [$\Delta\nu(C \equiv C)$] resulting from one-electron oxidation. The corresponding data for [M($C \equiv CC_6H_4$ -4-X)(dppe)Cp*] (M = Fe or Ru) are given in Table 5. In some cases more than one band is observed for the $\nu(C \equiv C)$ resonance, generally ascribed to Fermi coupling,²⁸ and therefore the precise magnitude of $\Delta\nu(C \equiv C)$ is somewhat debatable.

Comparing first IR data from across the series of neutral alkynyl complexes $[M(C \equiv CC_6H_4-4-X)(dppe)(\eta-L)]$ (M = Mo, L = C₇H₇; M = Fe or Ru, L = Cp*) (Tables 4 and 5) reveals that for any given substituent X, the $\nu(C \equiv C)$ values reflect the nature of the metal fragment, with the band being

Table 4. Infrared Spectroscopic Data for the Alkynyl Complexes $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]^{n+}$

	n = 0	n = 1	$\Delta \nu (C \equiv C)$	ref
$2a^a$	2045	2032	-13	14
$\mathbf{2b}^{a}$	2057	2044	-13	14
$2c^b$	2057	2009	-48	this work
$2\mathbf{d}^{c,d}$	2020	not obsd	n/a	this work
$2e^b$	2055	1996	-59	this work
$2\mathbf{f}^{b}$	2055	2011	-44	this work
$2g^c$	2050	2017	-33	this work
$2\mathbf{h}^b$	2047	2033	-14	this work
2i ^{c,e}	2030, 1993	2031	-1	this work

^{*a*} Data for n = 1 from isolated sample in CH₂Cl₂. ^{*b*} Spectroelectrochemical measurement in 0.1 M NBu₄PF₆/THF. ^{*c*} Spectroelectrochemical measurement in 0.1 M NBu₄PF₆/CH₂Cl₂. ^{*d*} Also ν (C=O) 1659 (n = 0), 1694 (n = 1) cm⁻¹. ^{*e*} Also ν (C=O) 1706 (n = 0), 1721 (n = 1) cm⁻¹.

Table 5. Infrared Spectroscopic Data for the Alkynyl Complexes $[M(C \equiv CR)(dppe)Cp^*]^{n+}$ (M = Fe or Ru)

		M = Fe		N	$\Lambda = Ru$	
R	n = 0	n = 1	∆ν- (C≡C)	n = 0	n = 1	∆ν- (C≡C)
C_6H_5	2053 ^{<i>a</i>}	2021, 1988 ^b	е	2072 ^c	1930	-141
C ₆ H ₄ -4- Me	2056 ^b	1994 ^b	-62	2073 ^c	1928	-145
C ₆ H ₄ -4- OMe	2058 ^b	1988 ^b	-70	2074 ^{<i>d</i>}	1929	-145
C ₆ H ₄ -4- NH ₂	2060 ^b	1988sh, 1962 ^b	е	2075 $2050 \mathrm{sh}^d$	1940	-135
C ₆ H ₄ -4- NO ₂	2036, 2008 ^b	2038 ^b	е	2048 2017 ^d	1942	-106

^{*a*} Ref 10. ^{*b*} Ref 8. ^{*c*} Ref 12. ^{*d*} Ref 11. ^{*e*} $\Delta\nu$ (C=C) in Fe series not quoted due to multiple ν (C=C) bands.

progressively shifted to lower wavenumber as the electrondonating ability of the metal fragment increases (e.g., X = Me, $\nu(C \equiv C)$ (cm⁻¹/CH₂Cl₂): M = Ru, 2073; M = Fe, 2056; M = Mo, 2050). Furthermore it is evident that the three systems are distinct in the magnitude of the shift in $\nu(C \equiv C)$ following one-electron oxidation, with the molybdenum complexes exhibiting the smallest negative shifts. Taking as an example X =Me, the respective shifts in $\Delta\nu(C \equiv C)$ are M = Ru, -145 cm⁻¹; M = Fe, -62 cm⁻¹; and M = Mo, -33 cm⁻¹.

In summary, the electrochemical and spectroscopic properties of the $[Mo(C=CR)(dppe)(\eta-C_7H_7)]^{n+}$ complexes more closely resemble those of the Fe than the Ru series. The apparently limited Mo-alkynyl mixing cannot be accounted for by the simple analogies between the 3d and 4d transition

⁽²⁸⁾ Paul, F.; Mevellec, J.-Y.; Lapinte, C. J. Chem. Soc., Dalton Trans. 2002, 1783.

Table 6. Selected Bond Lengths and Bond Angles for 2A and [2A]⁺, Obtained at the BP86/SVP and B3LYP/SVP Levels

		2A	[2	$[\mathbf{A}]^+$
	BP86	B3LYP	BP86	B3LYP
	Bond Le	engths (Å)		
$\begin{array}{l} Mo-C_{\alpha}\\ C_{\alpha}-C_{\beta}\\ C_{\beta}-C_{(substituent)}\\ Mo-P \end{array}$	2.093 1.254 1.427 2.486 2.485	2.125 1.238 1.429 2.529 2.527	2.047 1.257 1.423 2.556 2.553	2.073 1.239 1.427 2.596 2.591
	Bond Ar	ngles (deg)		
$Mo-C_{\alpha}-C_{\beta}$ $C_{\alpha}-C_{\beta}-C_{(substituent)}$ $P-Mo-P$ $P-Mo-C_{\alpha}$ $Ct-Mo-C_{\alpha}^{a}$	177.8 179.7 78.8 83.5 77.2 127.6	177.6 179.8 78.6 84.2 77.7 127.4	176.9 178.7 79.5 82.8 77.3 130.3	176.5 179.5 79.1 83.1 77.5 129.9

 a Ct = centroid of the C₇H₇ ring.

series advanced to rationalize the differences between the group 8 systems. Therefore to understand further the predominantly metal-localized redox character of the [Mo- $(C \equiv CR)(dppe)(\eta - C_7H_7)$] system, a DFT analysis of $2a/[2a]^+$ was undertaken.

Electronic Structure Calculations. A computational study of the electronic structure of the model system $[Mo(C \equiv CPh)(dppe)(C_7H_7)]^{n+}$ (denoted 2A, $[2A]^+$ to distinguish the computational and experimental systems) was conducted at the DFT level. Starting from the crystallographic structure of 2a, full geometry optimizations were performed on 2A and [2A]⁺ using both the BP86 and B3LYP functionals and the Def2-SVP basis obtained from the Turbomole library.²⁹ For H, C, and P atoms, this constitutes an all-electron split valence plus polarization basis, while for Mo an effective core potential is applied to account for 28 core electrons (K, L, and M shells) with a split valence orbital set including a set of f-type polarization functions. This basis was also used to obtain IR frequencies and the UV/vis spectra (via time-dependent density functional theory, TD-DFT, as implemented in the Gaussian suite of programs³⁰).

There is good agreement between the crystallographically determined structures of $2a/[2a]^+$ and the DFT-optimized geometries; key variables from the DFT-optimized geometries are shown in Table 6. Comparing with the X-ray data



Figure 7. Energy (eV) of key molecular orbitals of **2A** (B3LYP/ SVP including PCM solvation in CH₂Cl₂).

and averaging over these structures we find an average absolute error in the bond lengths of 0.033 Å (BP86)/0.040 Å (B3LYP) and 1.3° in the angles for both functionals. The energies and composition of the key orbitals for **2A** (LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-18, and HOMO-19) are summarized in Table 7 and Figure 7; Figure 8 illustrates the plots of these frontier orbitals.

The structural and IR spectroscopic changes resulting from one-electron oxidation can be satisfactorily rationalized in terms of the properties of the HOMO of 2A (Figure 8c). The antibonding character of the HOMO with respect to the metal-alkynyl bond prescribes a shorter, stronger Mo- C_{α} bond on removal of an electron from 2A to form $[2A]^+$ (see Table 6). Conversely the alkynyl C=C bond is modestly weakened by removal of an electron from a HOMO that has alkynyl C=C bonding character but a relatively small population on the C_2 unit (see Table 7), and this is reflected in the small reduction in the $\nu(C=C)$ stretching frequency in the 17-electron radical [ν (C=C), cm⁻¹ (CH₂Cl₂), calculated: **2A**, 2048 (BP86)/2138 (B3LYP), **[2A**]⁺, 2008 (BP86)/2101 (B3LYP); experimental: 2a, 2045, [2a]⁺, 2032; the calculated values have not been scaled]. The B3LYP level predicts a reduction of 37 cm^{-1} , while the BP86 functional gives a reduction of 40 cm⁻¹; the absolute values predicted by the BP86 functional are in better agreement with experiment, but the trend is slightly better reproduced at the B3LYP level. A related DFT treatment of $[Ru(C \equiv CPh)(PH_3)_2Cp]$ reveals that the HOMO population at the C_2 unit is 38% (and 62% in total on the C_2 Ph ligand, cf. 2A, 25%), and these differences can clearly account for the much larger impact on $\nu(C \equiv C)$ of removal of an electron from the HOMO of the Ru system. The challenge however is to explain the contrasting population distribution in the HOMO of the Mo and Ru complexes, and this issue is addressed below.

A key feature of the electronic structure of **2A** is the strong δ -interaction between the metal d_{xy} and d_{x^2} -y² orbitals and the e₂ level of the C₇H₇ ring, evident from HOMO-1 and

⁽²⁹⁾ Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123. Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297. http://bases.turbo-forum.com/TURBOMO-LE_BASISSET_LIBRARY/tbl.html.

⁽³⁰⁾ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, ; Scalmani, M. G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev O; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Danneberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.

Table 7. Population Analysis (%) of Key Molecular Orbitals of 2A at B3LYP/SVP (including PCM solvation in CH₂Cl₂)

	fragment (excluding hydrogen atoms and Ph groups of dppe)						
orbital	Мо	C_7H_7	C ₂	C_6H_5	P ₂		
LUMO+1	10	14	7	10	6		
LUMO	14	34	2	2	12		
НОМО	62	4	16	9	3		
HOMO-1	24	37	25	6	4		
HOMO-2	47	37	6	2	3		
HOMO-18	9	60	0	0	8		
HOMO-19	11	33	12	2	9		
	(a) LUMO+1		(b) LUMO	J. G. J.			



Figure 8. LUMO+1, LUMO, HOMO, HOMO-1, HOMO-2, HOMO-18, and HOMO-19 of 2A at B3LYP/SVP (including PCM solvation in CH₂Cl₂) plotted as an isosurface of 0.04 au.

HOMO-2 (Figure 8d and e, respectively), which are strongly bonding between the metal and C_7H_7 ring. This represents a significant difference between the electronic structures of **2A** and its ruthenium analogue [Ru($C \equiv$ CPh)(dppe)Cp*] because δ -bonding has very limited importance in the ruthenium-cyclopentadienyl interaction. The origin of this effect can be traced to a stabilization of the ring orbitals of e_1 and e_2 symmetry as ring size increases, and this principle has been applied with some success in rationalizing the electronic structure and reactivity of sandwich complexes of the type [MCp(η -C₇H₇)] (M = Ti, Zr, V, Cr, Mo) and [M(η -C₇H₇)2]ⁿ (M = Th, Pa, U, Np, Pu, Am; n = -2, -1, 0,

(c) HOMO

+1; M = Ti, V, Cr, n = 0).³¹ Essentially, as ring size increases, the ring MOs move to lower energy,³² and therefore the principal frontier orbital metal-ring interactions

^{(31) (}a) Clack, D. W.; Warren, K. D. *Theor. Chim. Acta* 1977, 46, 313.
(b) Evans, S.; Green, J. C.; Jackson, S. E.; Higginson, B. J. Chem. Soc., Dalton Trans. 1974, 304. (c) Menconi, G.; Kaltsoyannis, N. Organometallics 2005, 24, 1189. (d) Tamm, M.; Kunst, A.; Bannenberg, T.; Herdtweck, E.; Schmid, R. Organometallics 2005, 24, 3163. (e) Glöckner, A.; Bannenberg, T.; Tamm, M.; Arif, A. M.; Ernst, R. D. Organometallics 2009, 28, 5866. (f) Li, J.; Bursten, B. E. J. Am. Chem. Soc. 1997, 119, 9021. (g) Wang, H.; Xie, Y.; King, R. B.; Schaefer, H. F.III. Eur. J. Inorg. Chem. 2008, 3698.

⁽³²⁾ Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. Inorg. Chem. 1976, 15, 1148.



Figure 9. HOMO and HOMO−1 of [Ru(C≡CPh)(PH₃)₂Cp] at B3LYP/3-21G* plotted as an isosurface of 0.04 au.¹²

involve the e_1 level for Cp but the e_2 level for C₇H₇. Confirmation that the e_1 level of the C₇H₇ ligand is moved to low energy in the half-sandwich system under investigation is provided by the identification of the π -interaction between the C₇H₇ MOs of e_1 symmetry and metal orbitals with mainly d_{yz} and d_{xz} character; these are much lower in the orbital manifold at HOMO-18 and HOMO-19 (Figure 8f and g). The perturbation in electronic structure introduced by metal-ring δ -bonding leads to a reordering of the metal d orbital manifold, resulting in a novel electronic structure for the half-sandwich, cycloheptatrienyl molybdenum system.

To understand the contrast between the electronic structure of **2A** and that of $[Ru(C \equiv CPh)(dppe)Cp^*]$, it is first necessary to specify the coordinate systems employed. In the familiar case of $[Ru(C \equiv CPh)(dppe)Cp^*]$, DFT calculations on the model complex $[Ru(C \equiv CPh)(PH_3)_2Cp]$ define the *z* axis along the Ru-C_{\alpha} (alkynyl) bond, determined by donation from the filled alkynyl σ orbital to the d_{z²} orbital on Ru.^{9,11,12} By contrast in **2A**, the *z* axis is directed along the line connecting the metal and the center of the C₇H₇ ring; the location of the d_{z²} orbital along this axis is evident in Figure 8c. For convenience, we have then assigned the plane passing through the Mo-C_{\alpha} (alkynyl) bond, the metal, and the center of the C₇H₇ ring as the *xz* plane.

Inspection of the MO energy level diagram for 2A (Figure 7) reveals two key points. First the HOMO in 2A is energetically discrete from both the LUMO and HOMO-1; this contrasts with the electronic structure of [Ru($C \equiv CPh$)(PH₃)₂Cp], where the HOMO and HOMO-1 are separated in energy by less than 0.1 eV and may interchange depending on the identity of the substituent on the alkynyl ligand.¹¹ The lowering in energy of HOMO-1 in 2A might be attributed to the additional δ -bonding between the metal d_{xy} orbital and the C₇H₇ ring. The second feature of interest lies in the directional properties of the HOMO; for [Ru($C \equiv CPh$)(PH₃)₂Cp] the HOMO/HOMO-1 (d_{xz} or d_{yz}) include the Ru-C_{α} (alkynyl) bond in the plane of the orbital (Figure 9).^{11,12} However, in the case of 2A, the HOMO, d_{z^2} , is approximately orthogonal to the Mo-C_{α} (alkynyl) bond.

Focusing now on the metal—alkynyl interaction, there are three important frontier components: a bonding interaction involving σ -donation from a filled orbital on the alkynyl ligand to an acceptor metal orbital and two antibonding, filled—filled π -interactions between the two orthogonal C=C π -bonds on the alkynyl ligand and filled metal d orbitals. For **2A** these latter π -interactions are clearly identified in the HOMO and HOMO-1 (Figure 8c and d) involving metal d_{z²} and d_{xy} orbitals. The σ -donation from the alkynyl ligand is much harder to trace, but the best candidate is shown in HOMO-19 (Figure 8g). In the ruthenium complex [Ru(C=CPh)(PH₃)₂Cp] the filled-filled π -antibonding interactions can also be found in the HOMO and HOMO-1 (d_{xz} or d_{yz} in the coordinate system of the cyclopentadienyl ruthenium complex). In both complexes, the HOMO and HOMO-1 are antibonding with respect to the metal-C_{α} (alkynyl) interaction but conversely possess alkynyl C=C bonding character.

The one-electron oxidation of the alkynyl complexes $[Mo(C \equiv CPh)(dppe)(\eta - C_7H_7)]$ and $[Ru(C \equiv CPh)(dppe)Cp^*]$ will result in a depletion of electron density in the HOMO (and to a lesser degree HOMO-1) and should therefore lead to strengthening of the metal alkynyl bond but weakening of the alkynyl C=C bond. However the extent of the change is strongly dependent on the effectiveness of the metal to alkynyl interaction in the HOMO and HOMO-1. In the ruthenium system, there is good overlap between the metal d_{xz} and d_{yz} with the orthogonal alkynyl π -bonds in the almost degenerate HOMO and HOMO-1. Conversely for $[Mo(C \equiv CPh)(dppe)(\eta - C_7H_7)]$, the metal-alkynyl interaction in the HOMO is diminished by symmetry constraints; the metal d_{z^2} orbital of the HOMO must tilt to achieve effective overlap with the alkynyl π orbital. While the d_{xv} orbital of the HOMO-1 of 2A does possess the correct symmetry for an effective metal-alkynyl interaction, this (in contrast to the Ru system) is significantly lower in energy and is also involved in strong metal to ring δ -bonding. Therefore, the redox-induced changes observed for [Mo- $(C \equiv CPh)(dppe)(\eta - C_7H_7)]$ are moderated by the confinement of the redox process essentially to a single orbital in which symmetry constraints limit the efficiency of the metal-alkynyl interaction.

In summary, the contrasting redox behavior of [Mo-(C=CPh)(dppe)(η -C₇H₇)] and [Ru(C=CPh)(dppe)Cp*] can be attributed to the very different electronic structures of the two systems. The strongly bonding interactions between molybdenum and the C₇H₇ ring lead to stabilization of the metal d_{xy} and d_{x²-y²}(e₂) and d_{xz} and d_{yz} (e₁) orbitals, leaving an energetically discrete HOMO with significant d_{z²} character. The redox process is therefore centered on an orbital with a symmetry-constrained interaction between the metal and the filled alkynyl π orbital such that redox-induced changes at the alkynyl ligand are relatively small. No such symmetry constraints operate for [Ru(C=CPh)(dppe)Cp*], where the d_{xz} and d_{yz} components of the almost degenerate HOMO and HOMO-1 overlap directly with the filled, orthogonal alkynyl π orbitals.

Finally we note that the novel electronic structure of the $Mo(dppe)(\eta-C_7H_7)$ system sets it apart in studies on the redox chemistry of metal complexes of carbon chain systems. DFT calculations on models for key, alternative half-sandwich

complex	n^{+}				
2a	0	32 700 (21 000)	27 000 (12 200)	18 900 (1000), br	
	+1	33 300 (15 600), br	28 300 (8400)	18 900 (2100), sh, 16 900 (4800)	12 300 (390), br
2b	0	33 900 (8400)	. ,		
	+1	33 900 (7100), sh		20 000 (720)	
2d	0	33 800 (26 800)	28 300 (18800)	18 700 (890), br	
	+1	30100 (19100), sh	21 600 (8000)	18 600 (3200), br	
2f	0	32 500 (17 600)	27 900 (11 100)	17 000 (650)	
	+1		28 200 (8600)	16 000 (5900)	12 400 (770)
2g	0	32 680 (18 300)	27 100 (12800)	19 200 (800)	
	+1		28 250 (7800)	16 600 (5300)	12 500 (150)
$2\mathbf{i}^b$	0	31 700 (16 300)	22 200 (16200)	17 300 (2200)	
	+1		27 850 (10 500), 24 200 (6500)	18 600 (2400), 16 800 (3500)	11 800 (200)

 $^{a}\nu_{max}/cm^{-1}$ (ϵ/M^{-1} cm⁻¹) determined by spectroelectrochemical methods in 0.1 M NBu₄PF₆/CH₂Cl₂ unless stated otherwise. b 0.1 M NBu₄PF₆/THF.



Figure 10. Experimental UV/visible spectra of $2a/[2a]^+$ in CH₂-Cl₂/0.1 M NBu₄PF₆.

end-cap systems, Fe(dppe)Cp^{*},^{9,10} Re(NO)(PPh₃)Cp^{*},^{27b,33} and Mn(Me₂PCH₂CH₂PMe₂)Cp,³⁴ all reveal in-plane overlap between frontier metal d orbitals and filled carbon chain π orbitals in the HOMO. The unique orthogonal overlap between the d_{z²} orbital of the Mo(dppe)(η -C₇H₇) system and the filled π orbitals of a carbon chain and the consequential reduced metal–carbon interaction offers the potential to enhance the stability of highly reactive radicals of extended carbon chain complexes and to facilitate delineation of the separate metal and carbon chain components of a redox process.

UV/Visible Electronic Absorption Spectroscopy. The UV/ visible/NIR spectra of complexes (2a, 2b, 2d, 2f, 2g, 2i), chosen as being representative of the series, and the corresponding radicals, were recorded using spectroelectrochemical methods; the experimental spectra for 2a and [2a]⁺ are illustrated in Figure 10, and all data are summarized in Table 8.

The neutral 18-electron complexes all show strong absorptions below 30 000 cm⁻¹/333 nm) and at ca. 25 000 cm⁻¹/400 nm arising from transitions between the metal, phosphine, and cycloheptatrienyl ligands. A series of lower intensity bands around 17 000–19 200 cm⁻¹ (590–520 nm) are responsible for the varying blue-black, brown, or green color of the alkynyl complexes. The spectra of the aryl-alkynyl 17-electron radical cations $[2a^+]$, $[2f]^+$, $[2g]^+$, and $[2i]^+$ were characterized by a strong absorption band in the region 16 000–17 000 cm⁻¹ (625–590 nm) responsible for the



Figure 11. Simulated UV/vis spectrum of 2A (TD-DFT, B3LYP/SVP).

intense blue-purple or emerald green color of these systems. The energy of this visible transition is sensitive to the alkynyl substituent, being found at higher energy as the electronwithdrawing nature of the substituent is increased, consistent with assignment as a LMCT (aryl-alkynyl to metal) transition. In addition, very weak, low-energy bands are also observed in the spectra of the 17-electron radical cations around $12\,000\,\mathrm{cm}^{-1}$ (800 nm), which are likely d-d in origin. In the case of the non-aryl-substituted derivatives [**2b**]⁺ and [**2d**]⁺, the LMCT bands are weaker in intensity and shifted to higher energy, 18\,600-20\,000\,\mathrm{cm}^{-1} (537–500 nm), giving these species a distinct orange or red coloration. These differences between aryl- and alkyl-substituted alkynyls indicate a significant contribution from the aryl group to the LMCT processes in the former.

To provide a more detailed assignment of the electronic transitions that occur in these complexes, a TD-DFT study was undertaken on $2A/[2A]^+$. TD-DFT calculations were performed for the first 100 excited states for 2A and $[2A]^+$, and the effect of solvent (CH₂Cl₂) was included using the polarizable continuum model. Calculated oscillator strengths were then used to simulate³⁵ spectra in the region 14 000–40 000 cm⁻¹ (700–250 nm). Simulated spectra for 2A and $[2A]^+$ are shown in Figures 11 and 12.

For the 18-electron complex **2A**, both observed and simulated spectra feature two significant absorption maxima

⁽³³⁾ Jiao, H.; Costuas, K.; Gladysz, J. A.; Halet, J.-F.; Guillemot, M.;
Toupet, L.; Paul, F.; Lapinte, C. *J. Am. Chem. Soc.* 2003, *125*, 9511.
(34) Venkatesan, K.; Blacque, O.; Berke, H. *Dalton Trans.* 2007, 1091.

⁽³⁵⁾ O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. J. Comput. Chem. 2008, 29, 839.



Figure 12. Simulated UV/vis spectrum of $[2A]^+$ (TD-DFT, B3LYP/SVP).

below 400 nm (25000 cm⁻¹). The dominant states that contribute to these bands in 2A appear at 337 nm (29700 cm^{-1}) and 375 nm (26 670 cm^{-1}), but there are close lying adjacent states (with smaller but significant oscillator strengths) that shift the band centers to lower wavelengths. The state at 375 nm is composed of many orbital transitions, but the principal component, accounting for 17% of the wave function, is a transition from the HOMO to a highlying virtual orbital (LUMO+10), which corresponds to the transfer of electron density from the metal to the phenyl ring of the C=CPh unit. The only other excitations that carry a weight of >5% in the final wave function are a transition from HOMO-2 to LUMO, with a weight of 7% (this corresponds to a transfer of electron density from the Mo to the P atoms of the dppe unit) and a transition (weight 6%) from the HOMO to the phenyl rings of the dppe unit. The state at 337 nm arises principally due to transfer of electron density from the Mo(η -C₇H₇) unit to the dppe unit; there is very little weight for any transitions corresponding to the phenyl ring of the C=CPh unit. Finally, there is a band centered at 546 nm (18 300 cm^{-1}) responsible for the brown color of the complex, 31% of which comes about from an excitation from the HOMO (Figure 8c) to the LUMO+1 (Figure 8a).

As noted above, the experimental UV/vis spectra of the oxidized aryl-alkynyl complexes each feature an intense absorption in the region $16000-17000 \text{ cm}^{-1}$ (625–590 nm) (Figure 10). The simulated spectrum of $[2A]^+$ (Figure 12) shows a similar band centered on a transition at 582 nm ($2a^+$, experimental value 592 nm). This state is dominated by a single transition (weight 85%) that corresponds to an excitation within the β -spin orbital manifold of HOMO–2→ LUMO, but it should be noted that the spatial form of the β -spin LUMO is effectively that of the SOMO (α -spin). The orbitals involved are shown in Figure 13 and suggest that this transition corresponds to a transfer from the phenyl ring of the C≡CPh unit to the Mo(η -C₇H₇)C≡C− moiety, thus supporting the experimental LMCT assignment of the transition.

The band at 374 nm is dominated (30%) by an excitation from HOMO-2 to LUMO+1 within the α -spin orbital manifold as shown in Figure 14 and appears to indicate transfer from a Mo-C₇H₇ unit to the alkynyl ligand.

EPR Investigations. The well-resolved, isotropic character of the X-band EPR solution spectra of the 17-electron

radicals [MoX(dppe)(η -C₇H₇)]⁺ has been the focus of several previous reports, ^{14,36} and the DFT treatment, outlined below, now permits a much clearer rationalization of these results. Figure 15 illustrates the calculated unpaired spin density distribution in [**2A**]⁺ together with Mulliken spin densities. It is clear that unpaired spin density is located principally at the Mo center in a metal-based orbital with a significant d_{z²} contribution; this is consistent with the distinctly isotropic character of the experimental EPR spectra and in agreement with previous predictions for these complexes.³⁷

Two new experimental investigations have been undertaken in the current work. First, EPR spectra of a series of 17-electron alkynyl radicals $[Mo(C=CR)(dppe)(\eta-C_7H_7)]^+$, selected to encompass a wide range of R substituents, were recorded in fluid solution in dichloromethane at 243 K (on an isolated sample, [2a][BF₄], or by generation *in situ* on addition of [FcH][PF₆] to samples of 2d, 2f, 2g, and 2i). A typical spectrum (as a second derivative) is presented in Figure 16, and Table 9 summarizes experimental solution isotropic g values and hyperfine coupling parameters (confirmed by simulation); very little variation is observed with change in the identity of R.

Second we have recorded the W-band, solid-state spectrum (Figure 17) of an isolated sample of [**2a**][BF₄] and obtained, for the first time, anisotropic *g* values for an alkynyl complex of this type ($g_1 = 1.9992$, $g_2 = 1.9958$, $g_3 = 1.9892$; $\Delta g = g_1 - g_3 = 0.010$). These data, which complement reports for the related systems [MoX(dppe)(η -C₇H₇)]⁺ (X = F, NCO, NCS, CN) obtained at the Q-band,³⁶ reveal very small *g* value anisotropy, in marked contrast to complexes of the type [M(C=CR)(dppe)Cp*]⁺ (M = Fe or Ru), which exhibit much larger *g* value anisotropy (R = Ph; M = Fe, $\Delta g = 0.489$;¹⁰ M = Ru, $\Delta g = 0.239$,¹¹ frozen solution, 80 K).

An extended DFT investigation on the 17-electron radical $[2A]^+$ was undertaken, leading to calculation of the unpaired spin density distribution as presented in Figure 15. For calculations of EPR g tensors and hyperfine coupling tensors, the Mo basis was changed to the all-electron TZVPP-All-S2 basis, again from the Turbomole library.²⁹ In the allelectron calculations, s-type functions on all atoms were uncontracted. Convergence of the EPR parameters was checked by the inclusion of additional tight s functions (the exponents being obtained in geometric progression) on all atoms. Typically it was found that the inclusion of two additional sets of s functions was sufficient, since any further addition produced changes of less than 1 MHz (0.36 G) in the computed hyperfine tensors. The g tensor of $[2A]^+$ was calculated using gauge-including atomic orbitals (GIAO) and the B3LYP functional as implemented in the Gaussian suite of programs.³⁰ Although the g tensor is thought to show only a weak gauge dependence, the GIAO calculations reported here are rigorously gauge independent; however in the implementation used the spin-orbit operator is approximated by a one-electron operator with a scaled effective charge to account for the screened nuclear charge. The calculated components of the g tensor obtained were $g_1 =$ 2.0078, $g_2 = 1.9996$, $g_3 = 1.9792$, giving $g_{iso} = 1.9955$

⁽³⁶⁾ Aston, G. M.; Badriya, S.; Farley, R. D.; Grime, R. W.; Ledger, S. J.; Mabbs, F. E.; McInnes, E. J. L.; Morris, H. W.; Ricalton, A.; Rowlands, C. C.; Wagner, K.; Whiteley, M. W. J. Chem. Soc., Dalton Trans. **1999**, 4379.

⁽³⁷⁾ Rieger, P. H. Coord. Chem. Rev. 1994, 135/136, 203.



Figure 13. β -Spin orbital transition in [2A]⁺ that gives rise to the band calculated at 582 nm.



Figure 14. α -Spin orbital transition in [2A]⁺ that gives rise to the band calculated at 374 nm.



Figure 15. PBE0 spin density of $[2A]^+$ shown as an isosurface of 0.004 au. For clarity the atoms of the dppe unit are shown as wireframe only.



Figure 16. Fluid solution (CH₂Cl₂, 243 K), second-derivative X-band EPR spectrum of $[Mo(C \equiv CC_6H_4-4-Me)(dppe)(\eta-C_7H_7)][PF_6], [2g][PF_6].$

(experimental: $g_1 = 1.9992$, $g_2 = 1.9958$, $g_3 = 1.9892$, $g_{iso} = 1.9947$). To assess the effect of the choice of spin-orbit operator, we performed additional calculations of the *g* tensor using a mean field spin-orbit operator, which includes the effect of the two-electron spin-orbit integrals in an averaged way. Center of charge coordinates (which should minimize the gauge dependence) were used without the GIAO, as implemented in the ORCA program.³⁸ The

Table 9. EPR Data for the 17-Electron Radicals $[Mo(C=CR)(dppe)(\eta-C_7H_7)]^{+a}$

	[-··=•(=		///]	
	$A_{\rm iso}({\rm Mo})$	$a_{\rm iso}(^{31}{\rm P})$	$a_{\rm iso}(^{1}{\rm H})$	$g_{\rm iso}$
[2a] ⁺	31.3 ^b	22.6	4.3	1.996
[2d] ⁺	31.3	23.3	4.5	1.996
[2f] ⁺	31.3	22.1	4.2	1.995
$[2g]^+$	31.3	22.1	4.3	1.995
[2i] ⁺	31.3	22.8	4.3	1.996

^{*a*}X-band solution spectra in CH_2Cl_2 at 243 K; hyperfine couplings in gauss. ^{*b*} A_{iso} (Mo) value differs slightly from that reported (34.8) in ref 36. The revised value gives an enhanced fit to the positions of the Mo satellites.

values obtained were $g_1 = 2.0052$, $g_2 = 1.9997$, $g_3 = 1.9881$, giving $g_{iso} = 1.9977$. The two schemes used give a difference of some 2200 ppm in the value of g_{iso} . Table 10 compares the calculated g values with those from experiment and indicates that the use of the mean field spin—orbit operator is superior in predicting the components of the **g** tensor even though the isotropic value is less well reproduced.

The evaluation of the hyperfine tensors requires some careful comment. For the Mo atom, in addition to the isotropic Fermi contact (FC) term, it is important to include the spin-orbit contributions and relativistic effects. We performed calculations with the B3LYP and PBE0 functionals. We found the PBE0 functional to be slightly superior,

⁽³⁸⁾ Neese, F. ORCA, An Ab Initio, Density Functional, and Semiempirical Program Package, version 2.6, Rev. 35; Univ. Bonn: Bonn, 2008.



Figure 17. Solid-state W-band EPR spectrum of $[Mo(C \equiv CPh)(dppe)(\eta-C_7H_7)][BF_4], [2a][BF_4].$

 Table 10. Errors in the Components of g for $[2A]^+$ Obtained with the Two Computational Procedures Used

	GIAO + scaled Z one-electron spin-orbit operator	center of charge coordinates + mean field spin-orbit operator
Δg_1	0.0086	0.0060
Δg_2	0.0038	0.0039
Δg_3	0.0100	-0.0011
Δg_{iso}	0.0008	0.0030

overall, and the hyperfine couplings we report refer exclusively to this functional. The experimentally assigned isotropic hyperfine splitting for Mo (Table 9) is 31.3 G. Calculating just the FC term gives 22.4 G; adding the spin-orbit contribution of 3.2 G gives $A_{iso}(Mo) = 25.6$ G, which is our best nonrelativistic value. Adding relativistic effects via the ZORA approach changes the FC term to 26.8 G. Fully uncontracting all basis functions changes the FC term only a small amount to 27.4 G and the spin-orbit term changes to 3.0 G, indicating that our approach of uncontracting only the s functions is valid. Our best estimate becomes $A_{iso}(Mo) = 30.4$ G. While relativistic and spin-orbit contributions are important for $A_{iso}(Mo)$, they contribute negligibly to the hyperfine interactions of the other atoms. For example, taking the heaviest of the remaining atom types, P, we find that the spin-orbit contribution to $a_{\rm iso}(P)$ is < 0.1 G and the inclusion of relativistic effects changes $a_{iso}(P)$ by < 0.7 G. Thus in discussing the hyperfine couplings of all atoms except Mo, our values refer to the FC term alone evaluated in a nonrelativistic PBE0 calculation. Figure 18 summarizes the principal hyperfine couplings. In the X-band solution EPR experiment the hyperfine couplings for the P atoms of dppe are averaged, whereas in the calculations the static structure gives slightly inequivalent P atom environments. The averaged calculated value is $a_{iso}(P) = 23.8 \text{ G}$ (experiment $a_{iso}(P) = 22.6 \text{ G}$). Similarly, the protons of the C₇H₇ ring give an averaged $a_{iso}(H) = 3.9 \text{ G}$ (experiment $a_{iso}(H) = 4.3$ G). The remaining a_{iso} values shown in Figure 18 are not resolved under current experimental conditions. The values we are able to compare with experiment are reproduced within about 1 G, and we expect that the remaining a_{iso} have a similar reliability.

Conclusions

The alkynyl complexes $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]^{n+}$ (*n* = 0 or 1) feature occupied frontier orbitals that are essentially metal-localized. Experimentally this is manifest



Figure 18. Calculated isotropic hyperfine coupling constants (G) of $[2A]^+$.

in the small change in the alkynyl stretching frequency resulting from one-electron oxidation, the relatively high stability of the 17-electron radical cations, $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]^+$, and the excellent resolution of hyperfine coupling observed in the solution EPR spectra. These experimental observations can be rationalized by electronic structure calculations, which establish a significant metal d₇₂ contribution both to the HOMO of 18-electron $[Mo(C=CR)(dppe)(\eta-C_7H_7)]$ and to the location of unpaired spin density in the corresponding radical. The electronic structure of $[Mo(C=CR)(dppe)(\eta-C_7H_7)]$, in which the metal d_{z2}-based HOMO is energetically well separated from HOMO-1, is in marked contrast to the analogous group 8 complexes [Ru(C=CR)(dppe)Cp*], for which the HOMO and HOMO-1 are almost degenerate. These differences in electronic structure can be attributed to a diversity in metal-ring bonding. Stabilization of the ring molecular orbitals with increase in ring size facilitates a strong δ -interaction between molybdenum and the C_7H_7 ligand, an effect not present in the RuCp* system. The perturbation introduced by metal-ring δ -bonding leads to a reordering of the metal d orbital manifold, resulting in very different electronic structures for the two series of complexes $[Mo(C \equiv CR)(dppe)(\eta - C_7H_7)]$ and $[Ru(C \equiv CR)(dppe)Cp^*]$, which, on first inspection, might appear to be closely analogous systems of the 4d metals Mo and Ru.

Experimental Section

General Procedures. The preparation, purification, and reactions of the complexes described were carried out under dry nitrogen using standard Schlenk techniques. Methanol was best available commercial grade or dried on an Innovative Technologies SPS-400 system, and deoxygenated thoroughly by sparging with dry nitrogen before use. The complex [MoBr(dppe)(η -C₇H₇)]·0.5CH₂Cl₂ was prepared by a published procedure.¹⁷ The alkynes HC=CFc, HC=CC₆H₄-4-CHO, HC=CC₆H₄-4-OMe, and HC=CC₆H₄-4-CO₂Me were prepared by standard methods^{39,40} or purchased from commercial sources (HC=CPh,

⁽³⁹⁾ Polin, J.; Schottenberger, H. Org. Synth. 1996, 73, 262.

⁽⁴⁰⁾ Lavastre, O; Ollivier, L.; Dixneuf, P. H.; Sinbandhit, S. *Tetrahedron* **1996**, *52*, 5495.

 $HC \equiv CBu^t$, $HC \equiv CCO_2Me$, $HC \equiv CC_6H_4$ -4- NH_2 , $HC \equiv CC_6H_4$ -4-Me). NMR spectra were recorded from CD₂Cl₂ solutions, unless otherwise stated, containing trace amounts of CoCp₂ to prevent accumulation of Mo¹ species by aerial oxidation, on Varian Inova 300 or 400 or Bruker DRX-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, and the Department of Chemistry, Durham University. Cyclic voltammograms were recorded ($\nu = 100 \text{ mV s}^{-1}$) from 0.1 M NBu₄PF₆, CH₂Cl₂ solutions ca. 1×10^{-4} M in analyte using a gastight single-compartment three-electrode cell equipped with a Pt disk working electrode, Pt wire counter electrode, and Pt wire pseudoreference electrode, and data collected on an Autolab PG-STAT 30 potentiostat. The working electrode was polished with alumina paste before each scan. All redox potentials are reported with reference to an internal standard of the ferrocene/ferrocenium couple (FcH/FcH⁺ = 0.00 V). Electrochemical measurements at subambient temperatures were performed in the same cell, cooled by immersion in an external bath. UV/vis/NIR and IR spectroelectrochemical experiments were performed at room temperature with an airtight OTTLE cell equipped with Pt minigrid working and counter electrodes, a Ag wire reference electrode, and CaF2 windows²⁵ 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 were carried out using Bruker WinEPR software (Bruker Biospin Ltd.).

Preparations. Preparation of $[Mo(C=CPh)(dppe)(\eta-C_7H_7)]$ (2a). A mixture of $[MoBr(dppe)(\eta-C_7H_7)]\cdot 0.5CH_2Cl_2$ (813 mg, 1.15 mmol), HC=CPh (587 mg, 5.75 mmol), and KOBu^t (387 mg, 3.45 mmol) in methanol (50 cm³) was heated at reflux for 3 h. The resulting deep brown precipitate was collected, washed with hexane, and dried *in vacuo*. The solid was dissolved in CH₂Cl₂ (ca. 5 cm³), loaded onto a hexane/alumina column, and eluted with CH₂Cl₂/hexane/acetone (45:45:10 v/v/v). The major brown band was collected and evaporated to dryness to give a deep brown solid, which was reprecipitated from CH₂Cl₂/hexane; yield: 425 mg (54%). ¹H NMR: δ 2.11 (m, 2H, CH₂), 2.49 (m, 2H, CH₂), 4.82 (t, 7H, $J_{HP} = 2.1$ Hz, C_7 H₇), 6.03 (d, 2H, J_{HH} 7 Hz, C=CPh_o), 6.74 (m, 1H, C=CPh_p), 6.84 (m, 2H, C=CPh_m), 7.33-7.85 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 64.6 (s, dppe). IR (CH₂Cl₂) ν (C=C) 2045 cm⁻¹. MALDI-MS (m/z): 687, [M]⁺; 586 [(M - C=CPh)]⁺. Anal. Calcd (%) for C₄₁H₃₆MoP₂: C, 71.7; H, 5.3. Found: C, 71.4; H, 5.2.

Preparation of [**Mo**(**C≡CBu**^t)(**dppe**)(*η*-**C**₇**H**₇)] (**2b**). This was prepared and purified in an identical fashion to **2a**, using HC**≡**CBu^t (870 mg, 10.60 mmol), [MoBr(dppe)(*η*-C₇H₇)]· 0.5CH₂Cl₂ (1.50 g, 2.12 mmol), and KOBu^t (0.71 g, 6.36 mmol). The product was obtained as a dark brown solid; yield: 430 mg (30%). ¹H NMR: δ 0.40 (s, 9H, Bu^t), 2.20 (m, 2H, CH₂), 2.60 (m, 2H, CH₂), 4.66 (s, 7H, C₇H₇), 7.25–7.82 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 66.2 (s, dppe). IR (CH₂Cl₂): ν(C**≡**C) 2057 cm⁻¹. MALDI-MS (*m*/*z*): 668, [M]⁺. Anal. Calcd (%) for C₃₉H₄₀MoP₂: C, 70.3; H, 6.1. Found: C, 70.3; H, 6.0.

Preparation of [Mo(C=CFc)(dppe) $(\eta$ -C₇H₇)] (2c). A warm (ca. 50 °C) solution of [MoBr(dppe)(η -C₇H₇)] · 0.5CH₂Cl₂ (100 mg 0.14 mmol) in methanol (20 cm³) was treated with HC=CFc (38 mg, 0.18 mmol), and the resulting mixture heated at reflux point for 90 min. The solution was allowed to cool to room temperature before addition of Na metal (100 mg, 4 mmol). The solution was allowed to stir for 20 min, after which time

effervescence had ceased, and the solvent was removed *in vacuo*. The solid residue was extracted with CH₂Cl₂ (5 cm³), the extracts were filtered, and the filtrate was taken to dryness *in vacuo* to give a dark-colored solid, which was washed with Et₂O (3×5 cm³) and hexane (3×5 cm³) or until the washings were colorless and dried to afford **2c** as a free-flowing brown powder; yield: 10 mg (9%). ¹H NMR: δ 2.17 (m, 2H, CH₂), 2.64 (m, 2H, CH₂), 3.29 (t, $J_{\text{HH}} = 2$ Hz, 2H, Cp_{β}), 3.60 (s, 5H, Cp), 3.69 (t, $J_{\text{HH}} = 2$ Hz, 2H, Cp_{α}), 4.71 (br, 7H, C₇H₇), 7.29–7.89 (m, 20H, Ph). ³¹P{¹H} NMR: δ 65.6 (s, dppe). MALDI-MS (*m*/*z*): 796, [M]⁺. Anal. Calcd (%) for C₄₅H₄₀FeMoP₂: C, 68.0; H, 5.0. Found: C, 68.4; H, 5.2.

Preparation of [**Mo**(**C≡CCO**₂**Me**)(**dppe**)(*η*-**C**₇**H**₇)] (**2d**). This was prepared and purified in an identical fashion to **2a**, using methyl propiolate (288 mg, 3.43 mmol) in place of HC**≡**CPh, [MoBr(dppe)(*η*-C₇H₇)]·0.5CH₂Cl₂ (808 mg, 1.14 mmol), and KOBu^t (211 mg, 1.88 mmol). The product was obtained as a purple-red solid; yield: 240 mg (31%). ¹H NMR: δ 1.89 (m, 2H, CH₂), 2.35 (m, 2H, CH₂), 3.18 (s, 3H, Me), 4.71 (br, 7H, C₇H₇), 7.19−7.67 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 62.2 (s, dppe). IR (CH₂Cl₂): ν(C**≡**C) 2020, ν(C**≡**O) 1657 cm⁻¹. MAL-DI-MS (*m*/*z*): 669, [M]⁺. Anal. Calcd (%) for C₃₇H₃₄MoP₂: C, 66.5; H, 5.1. Found: C, 66.2; H, 5.1.

Preparation of [Mo(C≡CC₆H₄-4-NH₂)(dppe)(η-C₇H₇)] (2e). The reaction between [MoBr(dppe)(η-C₇H₇)] ·0.5CH₂Cl₂ (100 mg 0.14 mmol) and HC≡CC₆H₄-4-NH₂ (27 mg, 0.23 mmol) was carried out in a manner similar to that described for **2c**, affording **2e** as a deep green solid; yield 40 mg (38%). ¹H NMR: δ 2.06 (m, 2H, CH₂), 2.48 (m, 2H, CH₂); 3.40 (s, 2H, NH₂), 4.75 (t, *J*_{PH} = 2 Hz, 7H, C₇H₇), 5.87 (d, (AB), 2H, *J*_{HH} ≈ 8 Hz, C₆H₄), 6.20 (d, (AB) 2H, *J*_{HH} ≈ 8 Hz, C₆H₄), 7.30−7.81 (m, 20H, Ph). ³¹P{¹H} NMR: δ 65.7 (s, dppe). IR (CH₂Cl₂): ν(C≡C) 2053. ES(+)-MS (*m*/*z*): 701 [M]⁺. HR ES(+)-MS (*m*/*z*): 703.14469 (MoNP₂C₄₁H₃₇ requires 703.14552).

Preparation of $[Mo(C \equiv CC_6H_4-4-OMe)(dppe)(\eta-C_7H_7)]$ (2f). A solution of $Me_3SiC \equiv CC_6H_4$ -4-OMe (29 mg, 0.23 mmol) and KF (26 mg, 0.452 mmol) in methanol (20 cm³) was treated with [MoBr(dppe)(η-C₇H₇)]·0.5CH₂Cl₂ (100 mg, 0.14 mmol) and NaPF₆ (25 mg, 0.151 mmol). The resulting solution was heated at reflux point for 90 min before the solvent was removed. The residue was washed with hexane $(2 \times 10 \text{ cm}^3)$ and Et₂O $(2 \times 10 \text{ cm}^3)$ cm³) or until the washings were clear. The remaining solid was extracted with CH₂Cl₂ (5 cm³) and cannula filtered into stirred hexane (15 cm³) to give 2f as a dark British racing green colored precipitate; yield: 40 mg (37%). ¹H NMR: δ 2.03 (m, 2H, CH₂), 2.50 (m, 2H, CH₂), 3.63 (s, 3H, OMe), 4.78 (br, 7H, C₇H₇), 5.96 (d, (AB), 2H, $J_{HH} \approx 9$ Hz, C₆ H_4), 6.40 (d, (AB), 2H, $J_{HH} \approx 9$ Hz, C₆ H_4), 7.29–7.83 (m, 20 H, Ph). ³¹P{¹H} NMR: δ 64.1 (s, dppe). IR (CH₂Cl₂): ν (C=C) 2051; ν (Ar) 1604 cm⁻¹. ES(+)-MS (m/z): 716, $[M]^+$. HR ES(+)-MS (*m*/*z*): 718.1446 (MoOP₂C₄₂H₃₈ requires 718.1466).

Preparation of [Mo(C≡CC₆H₄-4-Me)(dppe)(η-C₇H₇)] (2g). A mixture of [MoBr(dppe)(η-C₇H₇)] •0.5CH₂Cl₂ (1.46 g, 2.06 mmol), HC≡CC₆H₄-4-Me (720 mg, 6.20 mmol), and KOBu^t (485 mg, 4.32 mmol) in methanol (50 cm³) was heated at reflux for 2 h. The reaction mixture was cooled and reduced in volume to ca. 20 cm³. The deep brown precipitate was collected, washed with hexane, and dried *in vacuo*; yield: 1.123 g (78%). ¹H NMR: δ 1.97 (m, 2H, CH₂); 2.04 (s, 3H, C₆H₄CH₃); 2.38 (m, 2H, CH₂); 4.70 (br, 7H, C₇H₇); 5.81 (d, (AB), 2H, J_{HH} ≈ 8 Hz, C₆H₄), 6.54 (d, (AB), 2H, J_{HH} ≈ 8 Hz, C₆H₄); 7.20−7.71 (m, 20H, Ph). ³¹P{¹H} NMR (CDCl₃): δ 64.6 (s, dppe). IR (CH₂Cl₂) ν(C≡C) 2048 cm⁻¹; MALDI-MS (*m*/*z*): 703, [M]⁺. Anal. Calcd (%) for C₄₂H₃₈MoP₂: C, 72.0; H, 5.5. Found: C, 72.0; H, 5.4.

Preparation of [Mo(C=CC₆H₄-4-CHO)(dppe)(\eta-C₇H₇)] (2h). The reaction between [MoBr(dppe)(\eta-C₇H₇)] •0.5CH₂Cl₂ (100 mg, 0.14 mmol), KF (0.013 g, 0.225 mmol), and SiMe₃C= CC₆H₄-4-CHO (0.036 g, 0.180 mmol) in methanol (20 cm³) was carried out in a manner similar to that described for 2f, affording 2h as a dark purple solid; yield: 73 mg (68%). ¹H

Table 11. Crystal Data and Refinement Parameters for Complexes 2b, 2d, 2g, 2h, 2i, and [2b]⁺

	2b C ₃₉ H ₄₀ MoP ₂	$\begin{array}{c} \textbf{2d} \\ C_{37}H_{34}MoO_2P_2 \end{array}$	2g C ₄₂ H ₃₈ MoP ₂	2h C ₄₂ H ₃₆ MoOP ₂	2i C ₄₃ H ₃₈ MoO ₂ P ₂	[2b] ⁺ C _{39.38} H ₄₁ MoP ₂ BF ₄ Cl _{0.75}
mass	666.59	668.52	700.60	714.59	744.61	785.50
temperature (K)	293(2)	100(2)	100(2)	120(2)	120(2)	100(2)
cryst syst	triclinic	monoclinic	orthorhombic	triclinic	monoclinic	orthorhombic
space group	$P\overline{1}$	P2(1)/n	Pbca	$P\overline{1}$	$P2_1/c$	Pbca
a (Å)	9.4042(5)	8.4986(13)	9.3678(7)	9.7255(3)	21.834(2)	19.117(2)
$b(\mathbf{A})$	10.0595(5)	18.382(3)	17.8334(14)	10.1112(3)	9.4090(10)	27.208(4)
$c(\mathbf{A})$	17.0911(9)	19.712(3)	39.472(3)	18.3099(5)	17.5983(19)	55.768(8)
α (deg)	89.5460(10)	90	90	79.663(10)	90	90
β (deg)	88.0610(10)	95.361(2)	90	83.21(2)	109.75(3)	90
γ (deg)	82.4370(10)	90	90	70.905(10)	90	90
$V(Å^3); Z$	1601.85(14); 2	3066.1(18); 4	6594.2(9); 8	1670.40(8); 2	3402.7(6); 4	29006(7); 32
absorp coeff (cm^{-1})	5.36	5.65	5.25	5.22	4	5.54
θ range (deg)	2.04-26.39	1.52-26.35	2.06-28.32	1.13-30.00	2.32 - 27.50	1.29-21.97
limiting indices (h,k,l)	-11/11;	-10/10;	-12/12;	-13/13;	-18/28;	-20/19;
,	-12/12;	-22/22;	-22/23;	-14/14;	-12/12;	27/28;
	-21/21	-24/24	-51/52	-25/25	-22/2	-56/58
total reflns	12 830	24 108	54 369	22417	21 624	110 282
indep reflns, $I > 2\sigma(I)$	6462	6257	8042	9720	7802	17 696
R_1	0.0243	0.0276	0.0585	0.0344	0.0699	0.0601
wR_2	0.0614	0.0708	0.0659	0.0882	0.1522	0.0998
completeness to θ (%)	98.5	100	100	99.6	99.8	99.9

NMR: δ 2.13 (m, 2H, CH₂), 2.42 (m, 2H, CH₂), 4.83 (br, 7H, C₇H₇), 5.94 (d, (AB), 2H, J_{HH} \approx 8 Hz, C₆H₄), 7.31 (d, (AB), 2H, J_{HH} \approx 8 Hz, C₆H₄), 7.29–7.84 (m, 20H, Ph), 9.65 (s, 1H, CHO). ³¹P{¹H} NMR: δ 63.6 (s, dppe). IR (CH₂Cl₂): ν (C=C) 2023; ν (C=O) 1680 cm⁻¹. HR ES(+)-MS (*m*/*z*): 716.12860 (MoOP₂-C₄₂H₃₆ requires 716.12953).

Preparation of [Mo(C≡CC₆H₄-4-CO₂Me)(dppe)(η-C₇H₇)] (2i). The reaction between [MoBr(dppe)(η-C₇H₇)]·0.5CH₂Cl₂ (500 mg, 0.70 mmol) and HC≡CC₆H₄-4-CO₂Me (300 mg, 1.88 mmol) in methanol (100 cm³) was carried out in a manner similar to that described for 2c, with deprotonation being effected by addition of Na (250 mg, 10 mmol), affording 2i as a black solid; yield: 280 mg (50%). ¹H NMR: δ 2.14 (m, 2H, CH₂), 2.47 (m, 2H, CH₂), 3.80 (s, 3H, Me), 4.85 (br, 7H, C₇H₇), 5.37 (d, (AB), 2H, J_{HH} ≈ 5 Hz, C₆H₄), 7.50 (d, (AB), 2H, J_{HH} ≈ 5 Hz, C₆H₄), 7.35−7.85 (m, 20H, Ph). ³¹P{¹H} NMR: δ 64.9 (s, dppe). IR (CH₂Cl₂): ν(C≡C) 2027, 1991; ν(C≡O) 1702. ES(+)-MS (m/z): 744, [M]⁺. HR ES(+)-MS (m/z): 746.13946 (MoO₂-P₂C₄₃H₃₈ requires 746.14150).

Crystallography. X-ray crystal structures of $[Mo(C \equiv CBu^{t})-(dppe)(\eta-C_{7}H_{7})]$, **2b**, $[Mo(C \equiv CCO_{2}Me)(dppe)(\eta-C_{7}H_{7})]$, **2d**, $[Mo(C \equiv C-C_{6}H_{4}-4-Me)(dppe)(\eta-C_{7}H_{7})]$, **2g**, $[Mo(C \equiv CC_{6}H_{4}-4-CHO)(dppe)(\eta-C_{7}H_{7})]$, **2h**, $[Mo(C \equiv CC_{6}H_{4}-4-CO_{2}Me)(dppe)-(\eta-C_{7}H_{7})]$, **2i**, and $[Mo(C \equiv CBu^{t})(dppe)(\eta-C_{7}H_{7})][BF_{4}]$, $[2b]^{+}$, were obtained.

The majority of details of the structure analyses carried out on complexes 2b, 2d, 2g, 2h, 2i, and $[2b]^+$ are given in Table 11. Single crystals of the complexes were obtained as follows: 2b: vapor diffusion of pentane into a CH2Cl2 solution of the complex to give black, irregular shaped crystals; 2d: vapor diffusion of pentane into a CH₂Cl₂ solution of the complex to give red-brown plates; 2g: vapor diffusion of pentane into a toluene solution of the complex to give brown plates; 2h: vapor diffusion of diethyl ether into a CH₂Cl₂ solution of the complex to give deep purple plates; 2i: vapor diffusion of diethyl ether into a CH₂Cl₂ solution of the complex to give green plates; and $[2b]^+$: vapor diffusion of diethyl ether into a CH₂Cl₂ solution of the complex to give orange-brown plates. In all cases the X-ray data were collected using graphite-monochromated Mo Ka $(\lambda = 0.7103 \text{ Å})$ radiation. With the exception of **2h** and **2i**, data collection, cell refinement, and data reduction were carried out with Bruker SMART and Bruker SAINT software; SHELXS-9741 was employed for the computing structure solution and SHELXL-9742 for the computing structure refinement, and an absorption correction was applied with the aid of the SADABS program.⁴³ Diffraction data for 2h and 2i were collected on a Bruker 3-circle diffractometer with a SMART 6K area detector; reflection intensities were integrated using the SAINT V6.45 program, and a numerical absorption correction was applied. All structures were solved by direct methods with refinement by full-matrix leastsquares based on F^2 against all reflections. With the exception of [2b][BF₄], all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions. In the case of [2b][BF₄] the asymmetric unit contains four crystallographically independent pairs of ions and 1.5 molecules of CH₂Cl₂, and the crystal diffracted very weakly so the data were cut at 0.95 Å resolution. One phenyl ring was constrained to a regular hexagon with restraints also applied to some geometric parameters. The key Mo-C_{α} distances (Å) in the four independent cations [2b]⁺ in the lattice are 2.070(11), 2.076(11), 2.050(13), and 2.067(13).

Electronic Structure Calculations. Electronic structure calculations were carried out on 2A and the corresponding cation, $2A^+$. Starting from the crystallographic structure of 2A, full geometry optimizations were performed on 2A and 2A⁺ using the Def2-SVP basis obtained from the Turbomole library.²⁹ For H, C, and P atoms, this constitutes an all-electron split valence plus polarization basis, while for Mo an effective core potential is applied to account for 28 core electrons (K, L, and M shells) with a split valence orbital set including a set of f-type polarization functions. This basis was also used to obtain IR frequencies and the UV/vis spectra (via timedependent density functional theory). For calculations of EPR gtensors and hyperfine coupling tensors, the Mo basis was changed to the all-electron TZVPP-All-S2 basis, again from the Turbomole library.²⁹ In the all-electron calculations, s-type functions on all atoms were uncontracted. Convergence of the EPR parameters was checked by the inclusion of additional tight s functions (the exponents being obtained in geometric progression) on all atoms. Typically it was found that the inclusion of two additional sets of s functions was sufficient, since any further addition produced changes of less than 1 MHz (0.36 G) in the computed hyperfine tensors.

DFT calculations were performed in the generalized gradient approximation (GGA) with the BP86 exchange-correlation functional.⁴⁴ For the TD-DFT, g tensor, and hyperfine tensor

⁽⁴²⁾ Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen: Germany, 1997.

⁽⁴³⁾ Sheldrick, G. M. SADABS, an Empirical Absorption Corrections Program; Universität Göttingen: Germany, 1997.

tre (44) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

⁽⁴¹⁾ Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution; Universität Göttingen, Germany, 1997.

calculations, the B3LYP hybrid exchange–correlation functional⁴⁵ was used. Hybrid functionals are generally found to give better predictions for UV/vis spectra and EPR parameters. For the latter, the PBE0 functional⁴⁶ was also used since this functional was designed for use in calculations of magnetic properties.

The IR frequencies were calculated from analytic second derivatives using the Gaussian suite of programs.³⁰ For g tensor calculations the gauge-including atomic orbitals (GIAO), as implemented in ref 30, were employed with a one-electron spin-orbit operator with a scaled charge. The ORCA program³⁸ was also used for g tensor calculation employing a mean field spin-orbit operator. In this work we are only interested in isotropic values of the hyperfine coupling constants. Accordingly, the Fermi contact term of the hyperfine interaction was evaluated and also the spin-orbit contribution. The ORCA

code³⁸ was used for the latter. The spin–spin dipole contribution is a traceless tensor and does not affect the isotropic hyperfine couplings. The influence of relativistic effects on the Mo hyperfine interaction was investigated within the zero-order regular approximation (ZORA),⁴⁷ including the picture change transformation necessary for the correct treatment of the FC term.⁴⁸

Acknowledgment. We thank the EPSRC for support of this work through grants EP/E025544/1 and EP/E02582X/1.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

(48) van Lenthe, E.; van der Avoird, A.; Wormer, P. E. S. J. Chem. Phys. **1998**, 108, 4783.

⁽⁴⁵⁾ Becke, A. D. J. Chem. Phys. 1993, 98, 5648.

⁽⁴⁶⁾ Adamo, C.; Barone, V. J. Chem. Phys. 1999, 110, 6158.

⁽⁴⁷⁾ van Lenthe, E.; Baerends, E. J.; Snijders, J. G. J. Chem. Phys. 1993, 99, 4597.