

Synthesis and characterization of novel neutral σ -alkynylcarbonylnitrosyl molybdenum(0) and tungsten(0) complexes. Crystal structure of $[\text{Mo}(\text{C}\equiv\text{C}^n\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ [dppe = 1,2-bis(diphenylphosphino)ethane]

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Received 9 October 1995

Abstract

σ -Alkynyl dicarbonyl complexes $[\text{M}(\text{C}\equiv\text{CR})(\text{CO})_2(\text{dppe})(\text{NO})]$ ($\text{M} = \text{Mo}$, $\text{R} = \text{H}$, ^tBu, ⁿPr, ⁱPr, Ph, CH_2OCH_3 , SiMe_3 ; $\text{M} = \text{W}$, $\text{R} = \text{H}$, ^tBu, ⁿPr) have been prepared by reaction of *mer*- $[\text{M}(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ with an equimolar amount of the acetylide salt $\text{M}'\text{C}\equiv\text{CR}$ ($\text{M}' = \text{Li}$, Na). The complexes $[\text{M}(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mo}$, W) and $[\text{Mo}(\text{CO})(\text{NCMe})_2(\text{dppe})(\text{NO})][\text{BF}_4]$ obtained by reaction of *mer*- $[\text{M}(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ with acetonitrile are suitable precursors for the synthesis of the complexes $[\text{M}(\text{CO})_2(\text{dppe})(\text{PR}_3)(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mo}$, W, $\text{PR}_3 = \text{PMe}_3$, PMe_2Ph) and $[\text{M}(\text{CO})(\text{NCMe})(\text{dppe})(\text{PR}_3)(\text{NO})][\text{BF}_4]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PPh_3 , $\text{P}(\text{OPh})_3$). The reaction of $[\text{Mo}(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})][\text{BF}_4]$ with $\text{NaS}(\text{o}-\text{C}_6\text{H}_4\text{Me})$ yields the neutral complex $[\text{Mo}(\text{S}(\text{o}-\text{C}_6\text{H}_4\text{Me}))(\text{CO})_2(\text{dppe})(\text{NO})]$. The crystal structure of $[\text{Mo}(\text{C}\equiv\text{C}^n\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ has been determined by X-ray diffraction methods. The Mo atom displays a distorted octahedral coordination involving the N and C atoms of the nitrosyl and the alkynyl ligands in the apical positions and the P atoms from the dppe chelating ligand and two C atoms from terminal carbonyl groups in the equatorial positions.

Keywords: Mo; W; Alkynyls; Carbonyls; Nitrosyls; X-ray structure

1. Introduction

While the synthesis and reactivity of transition metal alkynyl complexes has received increasing attention in recent years [1,2], few studies dealing with Group 6 terminal alkynyl complexes are known. Thus, the preparation of molybdenum $[\text{Mo}(\text{C}\equiv\text{CR})(\eta^5\text{-C}_5\text{H}_5)\text{LL}'_2]$ ($\text{L} = \text{L}' = \text{CO}$; $\text{R} = \text{Ph}$, C_4H_9) [3a,b], $\text{L} = \text{CO}$, $\text{L}' = \text{P}(\text{OMe})_3$, PMe_2Ph or $\text{L} = \text{L}' = \text{P}(\text{OMe})_3$; $\text{R} = \text{CMe}_3$ [3c] and tungsten $[\text{W}(\text{C}\equiv\text{C}-\text{C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{LL}']$ ($\text{L} = \text{L}' = \text{CO}$; $\text{R} = \text{Ph}$ [3b,4a,b], $\text{L} = \text{L}' = \text{P}(\text{OMe})_3$; $\text{R} = \text{Ph}$ [3c], $\text{L} = \text{CO}$, $\text{L}' = \text{PMe}_3$; $\text{R} = \text{C}_3\text{H}_5$ [4c]) complexes which contain the $[(\eta^5\text{-C}_5\text{H}_5)\text{M}]$ moiety, a widely used auxiliary for the stabilization of the alkynyl group in other transition metals [1a,4b,5], has been reported.

Moreover, Selegue and coworkers [6] synthesized, in 1991, the alkynyl/alkyne complex $[\text{W}(\text{C}\equiv\text{C}-\text{CMe}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\eta^2\text{-HC}\equiv\text{C}-\text{CMe}_3)]$ which allowed them to carry out the first alkynyl–vinylidene coupling reaction of a d^4 complex.

The oxidative addition of alkynes to *trans*- $[\text{M}(\text{N}_2)_2(\text{L}-\text{L})_2]$ has been used to prepare molybdenum and tungsten(II) and (IV) complexes like hydrido *cis*- $[\text{WH}(\text{C}\equiv\text{CCO}_2\text{Me})(\text{dppe})_2]$ [7a], dihydrido $[\text{MH}_2(\text{C}\equiv\text{CR})_2(\text{L}-\text{L})_2]$ ($\text{M} = \text{Mo}$ or W, $\text{R} = \text{Ph}$, CO_2Me or CO_2Et , $\text{L}-\text{L} = \text{dppe}$; $\text{M} = \text{Mo}$, $\text{R} = \text{Ph}$, $\text{L}-\text{L} = \text{depe}$ (1,2-bis(diethylphosphino)ethane)) [7a–c], trihydrido $[\text{MoH}_3(\text{C}\equiv\text{C}^t\text{Bu})(\text{dppe})_2]$ [7d] and dialkynyl complexes *trans*- $[\text{M}(\text{C}\equiv\text{CR})_2(\text{dppe})_2]$ ($\text{M} = \text{Mo}$ or W, $\text{R} = \text{Ph}$, CO_2Me or CO_2Et) [7a–c]. The displacement of triflate from $[\text{HC}\equiv\text{W}(\text{O}_2\text{SOCF}_3)(\text{dmpe})_2]$ by alkynyl lithium reagents allowed Hopkins and coworkers [8] to obtain

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recently a series of alkynyl-substituted methylidyne compounds of the type $[\text{HC}\equiv\text{W}(\text{C}\equiv\text{CR})(\text{dmpe})_2]$ ($\text{R} = \text{H}, \text{SiMe}_3, \text{Ph}, \text{C}_6\text{H}_4\text{-C}\equiv\text{C}^n\text{Pr}$; $\text{dmpe} = 1,2$ -bis(dimethylphosphino)ethane) [8]. However, the preparation of symmetrically and unsymmetrically substituted dimetallapolyynes $[\text{M}_2(\text{C}\equiv\text{CR})_4(\text{PMe}_3)_4]$ ($\text{M} = \text{Mo}$ or W , $\text{R} = \text{alkyl}, \text{aryl}$) [9a] and $[\text{W}_2(\text{C}\equiv\text{CR})_2\text{Cl}_2(\text{PMe}_3)_4]$ [9b] with quadruply bonded metals has also been reported by the same group.

With regard to d^6 complexes, only the following alkynyl derivatives have been described to the best of our knowledge: (a) anionic complexes, $[\text{M}(\text{C}\equiv\text{CR})(\text{CO})_5]^-$ ($\text{M} = \text{Cr}, \text{Mo}$ or W ; $\text{R} = \text{Me}, \text{Ph}$ [10], CMe_3 [11]), $[\text{M}(\text{C}\equiv\text{CPh})(\text{CO})_4(\text{PPh}_3)]^-$ ($\text{M} = \text{Mo}$ or W) [10] and *fac*- $[\text{W}(\text{C}\equiv\text{CR})(\text{CO})_3(\text{dppe})]^-$ ($\text{R} = \text{H}, \text{Me}, ^n\text{Bu}, \text{Ph}$) [12]; (b) neutral complexes $[\text{M}(\text{C}\equiv\text{CR})\text{L}_2(\eta^7\text{-C}_7\text{H}_7)]$ ($\text{M} = \text{Mo}$ or W ; $\text{L}_2 = 2\text{CO}, \text{R} = \text{Ph}$; $\text{L}_2 = \text{dppe}, \text{R} = \text{Ph}, ^t\text{Bu}, ^n\text{Bu}$) [13a–c], $[\text{M}(\text{C}\equiv\text{CR})(\text{CO})(\text{PR}_3)(\eta^7\text{-C}_7\text{H}_7)]$ ($\text{R} = \text{Ph}, ^t\text{Bu}$) [13d]. The oxidation of $[\text{Mo}(\text{C}\equiv\text{CR})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]$ with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{BF}_4]$ gives the alkynyl cations $[\text{Mo}(\text{C}\equiv\text{CR})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)][\text{BF}_4]$ ($\text{R} = \text{Ph}, ^t\text{Bu}$) which undergo coupling at the C_β carbon of the alkynyl ligand to afford the vinylidene-bridged dimeric products $[\text{Mo}_2(\text{dppe})_2(\eta^7\text{-C}_7\text{H}_7)_2(\mu\text{-C}_4\text{R}_2)]^{2+}$ [13b].

Following our interest in the chemistry of transition metal acetylide complexes [14], we report here the preparation of the first carbonylnitrosyl molybdenum(0) and tungsten(0) complexes containing alkynyl groups $[\text{M}(\text{C}\equiv\text{CR})(\text{CO})_2(\text{dppe})(\text{NO})]$ ($\text{M} = \text{Mo}$ or W) of the type shown in Scheme 1. Very recently, molybdenum complexes of this type have been postulated as intermediates in the synthesis of vinylidene complexes $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{C}(\text{Me})\text{R})(\text{CO})(\text{NO})]$ [15].

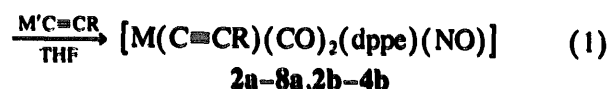
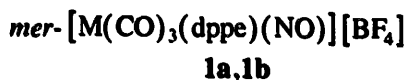
In contrast, the reactivity of complexes $[\text{M}(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mo}, \text{W}$) and $[\text{Mo}(\text{CO})_2(\text{NCMe})_2(\text{dppe})(\text{NO})][\text{BF}_4]$, which result from *mer*- $[\text{M}(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mo}$ (1a) or W (1b))

through CO ligand exchange by acetonitrile, towards typical nucleophiles such as phosphines, phosphites, acetylides and thiolates, is also reported. These substitution reactions lead to the preparation of the novel carbonyl substituted complexes shown in Scheme 1.

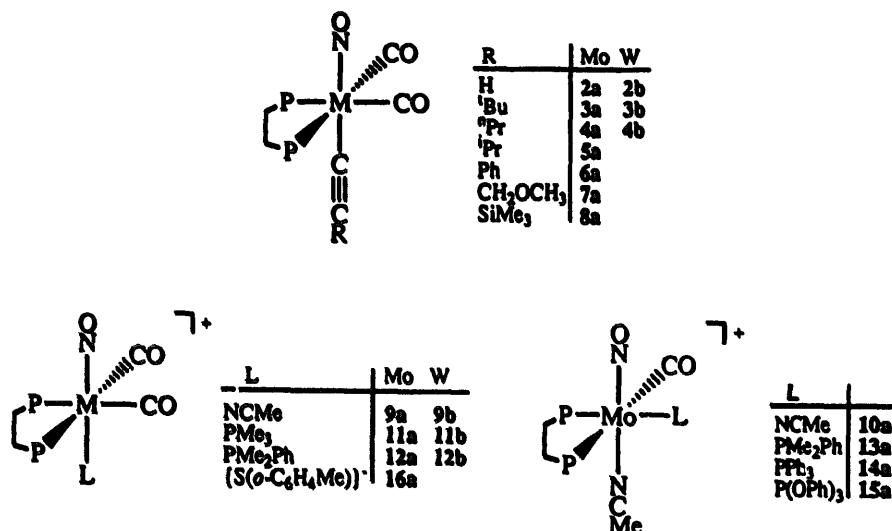
2. Results and discussion

2.1. Synthesis of the alkynyl molybdenum and tungsten complexes $[\text{M}(\text{C}\equiv\text{CR})(\text{CO})_2(\text{dppe})(\text{NO})]$ ($\text{M} = \text{Mo}; \text{R} = \text{H}$ (2a), ^tBu (3a), ^nPr (4a), ^iPr (5a), Ph (6a), $\text{CH}_2\text{-OCH}_3$ (7a), SiMe_3 (8a). $\text{M} = \text{W}; \text{R} = \text{H}$ (2b), ^tBu (3b), ^nPr (4b))

The reaction of *mer*- $[\text{Mo}(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ (1a) with an equimolar amount of the acetylide $\text{M}'\text{C}\equiv\text{CR}$ ($\text{M}' = \text{Li}, \text{Na}$) in THF at room temperature for 2–3 h affords, after chromatography, alkynyl molybdenum complexes 2a–8a. The tungsten complex 1b reacts much more slowly than the molybdenum analogue and requires higher temperatures and longer reaction times. Thus, complexes 2b, 3b, 4b have been similarly prepared after refluxing a THF solution of 1b with the corresponding acetylide during 5 h:



The progress of the reactions has been monitored by infrared spectroscopy in the carbonyl and nitrosyl region and by $^{31}\text{P}\{^1\text{H}\}$ NMR. The starting complex 1a or 1b rapidly disappear and a complex mixture of intermediate species is formed. In particular, ^{31}P NMR spectra



Scheme 1.

show characteristic resonances of complexes containing coordinated dppe in a monodentate fashion and other ones showing chemically inequivalent phosphorous atoms. The reactions are discontinued when the IR spectra mostly show a typical *cis*-dicarbonyl pattern. Working up the reaction mixtures give the alkynyl complexes in moderate yields. Although we have not studied the mechanism of the reactions, an isomerization process, associated with the *mer*-tricarbonyl to *cis*-dicarbonyl transformation, is taking place. This isomerization probably involves the opening of the chelating diphosphine, as can be observed in the ^{31}P NMR spectra.

These alkynyl complexes have also been synthesized in similar yields using the acetonitrile complexes $[\text{M}(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})][\text{BF}_4]$ (**9a**, **9b**) (see below) as precursors.

The novel alkynyl complexes are isolated as air-stable, yellow solids and have been characterized by elemental analysis, infrared and NMR (^1H , ^{31}P , ^{13}C) spectroscopy (details are given in the Experimental section). The infrared spectra show two strong $\nu(\text{CO})$ absorptions, as expected for a *cis* arrangement of the carbonyl ligands, along with the absorption due to the nitrosyl stretching vibration. The wavenumber depends on the substituent of the alkynyl group and the sequence appears to reflect the electron withdrawing nature of this group; however, the *cis* relationship between the alkynyl group and both CO and NO ligands makes these absorption differences rather small (see Table 1). The expected $\nu(\text{C}\equiv\text{C})$ absorption band is observed only for the complexes **3a–6a** and **3b–4b** as a very weak signal in the range 2094–2069 cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show a single resonance consistent with the chemical equivalence of the phosphorus atoms, in accordance with a *trans* arrangement of the alkynyl and nitrosyl groups and phosphorus and carbonyl ligands. The $J(\text{P}-^{183}\text{W})$ value of ca. 236 Hz in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2b–4b** is in the normal range for phosphorus nuclei

trans to carbonyl ligands [16]. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in CDCl_3 exhibit the expected signals for aromatic, methylene ($(\text{CH}_2)_2\text{P}_2$) and R hydrogens for the proposed structures. Thus, the methylene resonances in the proton NMR appear as two unresolved multiplets showing the $(\text{AB})_2\text{X}_2$ spin system consistent with the chemical inequivalence of the $(\text{CH}_2\text{H}_b)_2\text{P}_2$ protons in the chelated coordination of the phosphine. In the ^1H NMR spectra of **2a** and **2b** the ethynyl proton resonates at δ 1.36 (t, $^4J(\text{H}-\text{P}) = 3.4$ Hz) and 1.19 (t, $^4J(\text{H}-\text{P}) = 3.4$ Hz) ppm respectively. The signals for the C_α and C_β atoms of the acetylide group have been assigned on the basis of the chemical shift and C–P coupling constants. Thus, the spectra of the molybdenum complexes **3a**, **4a**, **5a** show the C_β to resonate as a singlet at δ 115–124 ppm and the C_α atom at higher field (105–110 ppm) as a triplet ($J(\text{C}_\alpha-\text{P}) = 16$ –17 Hz). This pattern is reversed in complexes **2a**, **6a**, **7a**, **8a** and the corresponding resonances are found at δ 101–122 ppm (singlet, C_β) and δ 118–148 ppm (triplet, $J(\text{C}_\alpha-\text{P}) = 16$ –17 Hz, C_α). Such a dependence of the chemical shifts on the nature of the alkynyl substituents has been previously observed by us [17] and is also found in the tungsten complex series (see Table 1).

Addition of electrophiles to the C_β of metal acetylides complexes has been described on many occasions [14a,c,18], and is perhaps the best entry into different types of vinylidene complexes. For instance, neutral vinylidene complexes $[\text{W}\{\text{C}=\text{C}(\text{R}^1)\text{R}^2\}(\text{CO})_3(\text{dppe})]$ ($\text{R}^1 = \text{R}^2 = \text{H}$, Me; $\text{R}^1 = \text{H}$, Me, $\text{R}^2 = \text{Ph}$) have been prepared by reaction of $[\text{W}(\text{C}\equiv\text{CR}^2)(\text{CO})_3(\text{dppe})]^-$ with the corresponding electrophile [12]. In our case, all attempts to prepare vinylidene complexes of molybdenum failed since the reaction of complexes **2a–7a** with HBF_4 and of complexes **3a**, **6a** with $\text{MeOSO}_2\text{CF}_3$ resulted in complex mixtures of unidentified species. The decreased reactivity could be a consequence of the presence of the nitrosyl group which results in less nucleophilicity of the C_β carbon atom.

Table 1
Selected IR ^a, $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR ^b data for the alkynyl complexes

Complex	IR		$^{31}\text{P}\{^1\text{H}\}$	$^{13}\text{C}\{^1\text{H}\}$		
	$\nu(\text{CO})$	$\nu(\text{NO})$		C_α	$^2J(\text{C}-\text{P})$	C_β
$[\text{Mo}(\text{C}\equiv\text{CH})(\text{CO})_2(\text{dppe})(\text{NO})]$ (2a)	2024 vs, 1958 vs	1647 s	48.78 s	118.47 t	16.2	101.03 s
$[\text{Mo}(\text{C}\equiv\text{C}^t\text{Bu})(\text{CO})_2(\text{dppe})(\text{NO})]$ (3a)	2021 vs, 1955 vs	1642 s	48.15 s	105.43 t	17.0	123.97 s
$[\text{Mo}(\text{C}\equiv\text{C}^n\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ (4a)	2021 vs, 1955 vs	1641 s	48.35 s	109.28 t	16.3	115.54 s
$[\text{Mo}(\text{C}\equiv\text{C}^t\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ (5a)	2021 vs, 1954 vs	1641 s	48.18 s	107.42 t	16.9	121.42 s
$[\text{Mo}(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{dppe})(\text{NO})]$ (6a)	2023 vs, 1957 vs	1647 s	48.78 s	^c		114.69 s
$[\text{Mo}(\text{C}\equiv\text{CCH}_2\text{OCH}_3)(\text{CO})_2(\text{dppe})(\text{NO})]$ (7a)	2023 vs, 1957 vs	1647 s	48.78 s	119.24 t	16.8	110.01 s
$[\text{Mo}(\text{C}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{dppe})(\text{NO})]$ (8a)	2027 vs, 1957 vs	1648 s	48.57 s	147.23 t	16.0	121.57 s
$[\text{W}(\text{C}\equiv\text{CH})(\text{CO})_2(\text{dppe})(\text{NO})]$ (2b)	2013 vs, 1940 vs	1637 s	34.90 s ^d	114.84 t	13.7	100.99 s
$[\text{W}(\text{C}\equiv\text{C}^t\text{Bu})(\text{CO})_2(\text{dppe})(\text{NO})]$ (3b)	2009 vs, 1936 vs	1632 s	34.82 s ^e	103.01 t	14.3	124.04 s
$[\text{W}(\text{C}\equiv\text{C}^n\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ (4b)	2010 vs, 1938 vs	1631 s	34.06 s ^f	106.62 t	14.2	115.56 s

^a In THF (cm^{-1}), abbreviations: vs, very strong; s, strong. ^b Spectra recorded in CDCl_3 , δ in ppm and J in Hz, abbreviations: s, singlet; t, triplet. ^c Overlapped by the PPh_2 carbons. ^d $J(\text{P}-\text{W}) = 236.5$ Hz. ^e $J(\text{P}-\text{W}) = 236.8$ Hz. ^f $J(\text{P}-\text{W}) = 236.2$ Hz.

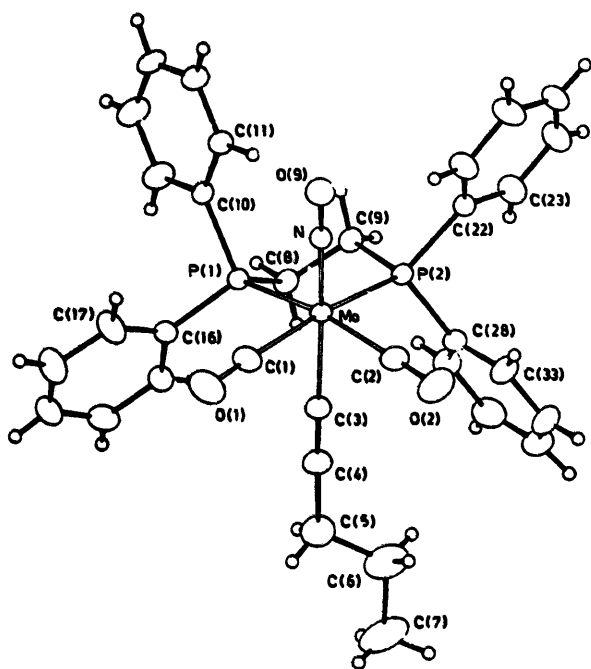


Fig. 1. View of the molecular structure of complex $[\text{Mo}(\text{C}\equiv\text{C}^n\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ (**4a**) with the atomic labelling scheme.

2.2. X-ray structure of the complex $[\text{Mo}(\text{C}\equiv\text{C}^n\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ (**4a**)

The structure of complex **4a** is shown in Fig. 1; selected bond distances and angles are given in Table 2. In the complex the Mo atom displays a distorted octahedral coordination with the nitrosyl group *trans* to the alkynyl one and the equatorial positions occupied by two P atoms from the chelating dppe ligand and two C atoms from terminal carbonyls. The Mo atom deviates by 0.2635(4) Å from the mean plane through the four equatorial atoms towards the N atom of the nitrosyl group, probably for electronic effects due to the partial Mo–N double bond character. It can be of interest to compare the main structural features of **4a** with those of the related Mo(0) complex $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]$ and of its one-electron oxidation product $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]^+[\text{BF}_4]^-$ [**13c**]. The Mo–P bond lengths in **4a**, 2.537(1) and 2.549(1) Å, are longer than those found in $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]$, 2.467(1) and 2.477(1) Å, as well as those in Mo–C(alkynyl), 2.182(4) against 2.138(5) Å. The longer Mo–P bond lengths in **4a** could be due to a weaker metal-to-ligand π back-donation, being the metal also involved in a π back-donation with the nitrosyl group. The value of the Mo–C(alkynyl) bond length in **4a** is the longest until now reported for the six structurally characterized molybdenum–alkynyl complexes quoted

in the Cambridge Structural Database and this lengthening could be due to the *trans* influence of the nitrosyl group. The alkynyl C≡C bond length in **4a**, 1.195(5) Å, is insignificantly shorter than in the tropylium complex, 1.205(6) Å, and the Mo–C–C angle, 176.4(3)°, is, as expected, close to 180°. In the cationic Mo(I) complex $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]^+$ the lengths of the Mo–P bonds, 2.528(3) and 2.538(2) Å, and that of the Mo–C(alkynyl) bond, 2.067(9) Å, are longer and shorter respectively with respect to those found in the neutral Mo(0) complex, reflecting a weaker π back-donation and a decreasing of the radius of the Mo atom in the formal higher oxidation state. Finally, in the Mo(II) complex *trans*- $[\text{Mo}(\text{C}\equiv\text{CPh})_2(\text{dppe})_2]$, the first structurally characterized alkynylmolybdenum complex [**7a**], the Mo–P bond lengths are 2.501(2) and 2.514(2) Å, and those of the Mo–C(alkynyl) and C≡C bonds are 2.093(8) and 1.237(12) Å respectively.

As regards the Mo–nitrosyl interaction in **4a**, both Mo–N bond length, 1.827(3) Å, and Mo–N–O angle, 175.2(2)°, are quite normal for a nitrosyl terminally bound to the Mo atom.

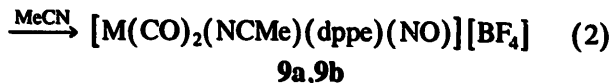
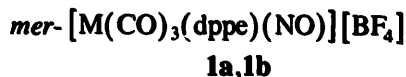
2.3. Synthesis of the complexes $[\text{M}(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mo}$ (**9a**), W (**9b**)) and $[\text{Mo}(\text{CO})(\text{NCMe})_2(\text{dppe})(\text{NO})][\text{BF}_4]$ (**10a**)

Cationic dicarbonyl complexes **9a** and **9b** have been prepared by heating a solution of the tricarbonyl complexes **1a** and **1b** in acetonitrile. The formation of **9a**

Table 2
Selected bond distances (Å) and angles (°) for complex **4a**

Mo–P(1)	2.537(1)	P(2)–C(22)	1.838(4)
Mo–P(2)	2.549(1)	P(2)–C(28)	1.824(4)
Mo–N	1.827(3)	O(1)–C(1)	1.131(5)
Mo–C(1)	2.041(4)	O(2)–C(2)	1.139(5)
Mo–C(2)	2.026(4)	O(3)–N	1.199(4)
Mo–C(3)	2.182(4)	C(3)–C(4)	1.195(5)
P(1)–C(8)	1.841(4)	C(4)–C(5)	1.481(6)
P(1)–C(10)	1.842(4)	C(5)–C(6)	1.492(9)
P(1)–C(16)	1.822(4)	C(6)–C(7)	1.518(9)
P(2)–C(9)	1.845(4)	C(8)–C(9)	1.526(6)
C(2)–Mo–C(3)	85.0(1)	P(1)–Mo–C(2)	164.8(1)
C(1)–Mo–C(3)	82.7(2)	P(1)–Mo–C(1)	91.8(1)
C(1)–Mo–C(2)	92.0(2)	P(1)–Mo–N	102.3(1)
N–Mo–C(3)	174.4(1)	P(1)–Mo–P(2)	79.6(1)
N–Mo–C(2)	92.2(1)	Mo–N–O(3)	175.2(3)
N–Mo–C(1)	92.5(1)	Mo–C(1)–O(1)	177.2(4)
P(2)–Mo–C(3)	84.4(1)	Mo–C(2)–O(2)	178.4(4)
P(2)–Mo–C(2)	93.5(1)	Mo–C(3)–C(4)	176.4(3)
P(2)–Mo–C(1)	165.5(1)	C(3)–C(4)–C(5)	176.8(4)
P(2)–Mo–N	100.7(1)	C(4)–C(5)–C(6)	114.2(4)
P(1)–Mo–C(3)	80.9(1)	C(5)–C(6)–C(7)	111.6(5)

occurs at 50°C (2.5 h) while refluxing is required for **9b** (5 h):



Monitoring the formation of **9a** by scanning the carbonyl-stretching region of the IR spectrum and by $^{31}\text{P}\{^1\text{H}\}$ NMR enabled us to detect a *cis*-dicarbonyl intermediate ($\nu(\text{CO})$ 2041 vs, 1968 vs, $\nu(\text{NO})$ 1694 cm^{-1} ; δ 32.14 d, 46.97 d ppm, $^2J(\text{P}-\text{P}) = 8.7$ Hz). These data are in agreement with the initial substitution of the carbonyls *trans* to each other by acetonitrile followed by isomerization of the resulting *cis*-dicarbonyl species. No similar intermediate could be detected in the case of **9b**.

The replacement of a second CO ligand with acetonitrile was accomplished by heating the complex **9a** in acetonitrile at reflux for 5 h to give complex **10a**. Attempts to form an analogous tungsten complex were unsuccessful.

Complexes **9a**, **9b** and **10a** are air-sensitive solids. They have been characterized by elemental analyses, conductance measurements, infrared and ^1H , ^{31}P , ^{13}C NMR spectroscopy (details are given in the Experimental section). The overall molecular geometry of **9a** and **9b** can be inferred from their IR and $^{31}\text{P}\{^1\text{H}\}$, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The infrared spectra of **9a** and **9b** show the expected two strong $\nu(\text{CO})$ absorptions typical for a *cis* arrangement of the carbonyl ligands, two very weak $\nu(\text{C}\equiv\text{N})$ absorptions characteristic of the coordinated acetonitrile ligands, as well as a broad $\nu(\text{B}-\text{F})$ absorption at ca. 1060 cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show a single resonance revealing that the two phosphorus atoms are equivalent in accordance with a *trans* arrangement of the acetonitrile and nitrosyl groups and phosphorus and carbonyl ligands. The $J(\text{P}-^{183}\text{W})$ value of 250 Hz is in the range typical for a phosphine *trans* to a carbonyl ligand (see above).

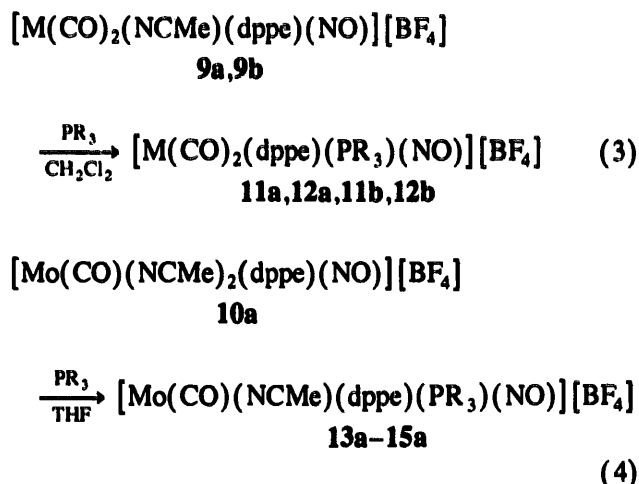
The structure of **10a** is proposed on the basis of the following data. Its IR spectrum exhibits a strong band at 1957 cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reflects the inequivalence of both phosphorus atoms since it consists of two doublets ($^2J(\text{P}-\text{P}) + ^3J(\text{P}-\text{P}) = 0.84$ Hz) at δ 40.89 and 66.26 ppm, the former being assigned to the phosphorus atom located *trans* to the carbonyl ligand in agreement with phosphorus resonances of complex **9a**. Owing to this phosphorus atom's inequivalence the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows carbonyl groups as a doublet of doublets at δ 226.37 ppm ($^2J(\text{C}-\text{P})$ (*trans*) = 48.9 and $^2J(\text{C}-\text{P})$ (*cis*) = 8.5 Hz). Finally, both

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data confirm the inequivalence of the acetonitrile ligands.

2.4. Reactivity of the complexes $[M(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})][\text{BF}_4]$ ($M = \text{Mo}$ (**9a**), W (**9b**)) and $[\text{Mo}(\text{CO})(\text{NCMe})_2(\text{dppe})(\text{NO})][\text{BF}_4]$ (**10a**)

While the complexes *mer*- $[M(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ (**1a**, **1b**) react with $\text{M}'\text{C}\equiv\text{CR}$ yielding the alkynyl derivatives (see above), their reaction with neutral phosphine ligands leads to mixtures of products whose identities depend largely on the solvent, along with considerable amounts of the polinuclear species [19]. We have found that complexes **9a**, **9b** and **10a**, containing labile acetonitrile ligands, are useful precursors of cationic dicarbonyl and monocarbonyl nitrosyl derivatives by reaction with neutral phosphine and phosphite ligands.

The addition of stoichiometric amounts of PMe_3 or PMe_2Ph to a dichloromethane solution of **9a** and **9b** leads, in high yield, to the formation of the corresponding cationic complexes $[M(\text{CO})_2(\text{dppe})(\text{PR}_3)(\text{NO})][\text{BF}_4]$ ($M = \text{Mo}$; $\text{PR}_3 = \text{PMe}_3$ (**11a**), PMe_2Ph (**12a**). $M = \text{W}$; $\text{PR}_3 = \text{PMe}_3$ (**11b**), PMe_2Ph (**12b**)). The reactions are carried out at room temperature (2 h) for **11a** and **12a** and reflux (5 h) for **11b** and **12b** (Eq. (3)). Complex **9a** is unreactive with PPh_3 or P(OPh)_3 in refluxing dichloromethane but **9a** reacts with stoichiometric amounts of PMe_2Ph , PPh_3 and P(OPh)_3 in refluxing THF (1–3 h) to give $[\text{Mo}(\text{CO})(\text{NCMe})(\text{dppe})(\text{PR}_3)(\text{NO})][\text{BF}_4]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$ (**13a**), PPh_3 (**14a**), P(OPh)_3 (**15a**)). These complexes **13a**, **14a** and **15a** can also be prepared by reaction of **10a** with the corresponding ligand in refluxing THF (Eq. (4)).



Complexes **11a**, **11b**, **12a** and **12b** are yellow, air-stable solids, whereas complexes **13a**–**15a** are yellow or red air-sensitive solids. They have been characterized by elemental analyses, conductance measurements, infrared, ^1H , ^{31}P and ^{13}C NMR spectroscopy (details are given in the Experimental section). The infrared spectra

of complexes **11a,b** and **12a,b** show the expected two strong $\nu(\text{CO})$ absorptions typical for a *cis* arrangement of the carbonyl ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra consists of a triplet and a doublet signals assigned to the phosphorus atom of the monodentate phosphine PR_3 and to the dppe phosphorus atoms respectively; the $J(\text{P}-\text{W})$ value of ca. 245 Hz for the phosphorus atoms of the dppe is in accordance with a *trans* arrangement of the dppe and the carbonyl ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **13a–15a** show an ABX pattern and the coupling constants confirm the phosphine or phosphite ligand to have a *trans* relationship with one of the dppe phosphorus; in addition $^{13}\text{C}\{^1\text{H}\}$ data also support such a structural arrangement

We have also examined the reaction of **9a** and **9b** with anionic ligands (see above). Thus, complex $[\text{Mo}(\text{S}(o\text{-C}_6\text{H}_4\text{Me})(\text{CO})_2(\text{dppe})(\text{NO}))]$ (**16a**) can be isolated in high yield from the reaction of **9a** and $\text{NaS}(o\text{-C}_6\text{H}_4\text{Me})$, which is prepared in situ from NaH and $\text{HS}(o\text{-C}_6\text{H}_4\text{Me})$.

3. Experimental details

All reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complexes $[\text{M}(\text{CO})_4(\text{dppe})]$ and *mer*- $[\text{M}(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mo}, \text{W}$) were prepared via a modification of previously published procedures [19,20] and details are given below. The ligand 1,2-bis(diphenylphosphino)ethane was prepared according to a published procedure [21]. $[\text{W}(\text{CO})_6]$, $[\text{Mo}(\text{CO})_6]$, $\text{MeOSO}_2\text{CF}_3$, $\text{HBF}_4 \cdot \text{OEt}_2$, and all the alkynes were purchased from Strem and Aldrich Chemical Co. and used without further purification.

Infrared spectra were recorded on a Perkin-Elmer 1720-XFT and a Nicolet FT 205 spectrometer. Electron impact mass spectra were obtained with a Hewlett-Packard 58971 instrument. The conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using CDCl_3 as solvent and SiMe_4 or 85% H_3PO_4 as standards.

3.1. Preparation of the complex $[\text{Mo}(\text{CO})_4(\text{dppe})]$

A mixture of $[\text{Mo}(\text{CO})_6]$ (1.32 g, 5 mmol) and dppe (2.0 g, 5 mmol) was heated under reflux in toluene (50 cm^3) for 4 h. The yellow solution was then evaporated to dryness and the resulting yellowish solid was washed with hexane ($3 \times 15 \text{ cm}^3$) and vacuum dried. Yield 95%. Identified by comparison with reported data [20].

3.2. Preparation of the complex $[\text{W}(\text{CO})_4(\text{dppe})]$

A mixture of $[\text{W}(\text{CO})_6]$ (1.00 g, 2.84 mmol) and dppe (1.20 g, 3 mmol) in toluene (50 cm^3) was heated at 170°C in a sealed evacuated tube over 10 h. The yellow solution was then evaporated to dryness and the resulting solid was washed with hexane ($3 \times 15 \text{ cm}^3$) and vacuum dried. Yield 95%. Identified by comparison with reported data [20b].

3.3. Preparation of the complexes *mer*- $[\text{M}(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mo}$ (**1a**), W (**1b**))

To a solution of the complex $[\text{Mo}(\text{CO})_4(\text{dppe})]$ (2 mmol) in toluene (50 cm^3)/methanol (7 cm^3) was added NOBF_4 (2 mmol) and the resulting suspension was stirred at room temperature. After 30 min an excess of NOBF_4 (1 mmol) was added and the mixture stirred for 2 h. Diethyl ether (50 cm^3) was added until no further solid was formed. The solution was decanted and the yellow solid washed with diethyl ether ($2 \times 20 \text{ cm}^3$) and vacuum dried. Identified by comparison with reported data for *mer*- $[\text{M}(\text{CO})_3(\text{dppe})(\text{NO})][\text{PF}_6]$ [19]. Yield (%); colour; conductivity (acetone, 20°C , $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$); IR (CH_2Cl_2 , $\nu(\text{C}=\text{O})$, $\nu(\text{N}=\text{O})$, cm^{-1}), and NMR spectroscopic data (^1H , $^{31}\text{P}\{^1\text{H}\}$) are as follows.

1a: 95; yellow; 125; 2103 m, 2035 vs, 1723 s. ^1H RMN: δ 3.13–3.41 (m, 4H, $\text{P}(\text{CH}_2)_2\text{P}$), 7.16–7.70 (m, 20H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ RMN: δ (32.95 d, $^3J(\text{P}-\text{P}) = 9.4$ Hz), 45.30 (d, $^3J(\text{P}-\text{P}) = 9.4$ Hz) ppm.

1b: 98; yellow; 125; 2098 m, 2021 vs, 1724 s. ^1H RMN: δ 3.23–3.5. (m, 4H, $\text{P}(\text{CH}_2)_2\text{P}$), 7.16–7.70 (m, 20H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 25.33 (s, $J(\text{P}-\text{W}) = 165.3$ Hz), 31.94 (s, $J(\text{P}-\text{W}) = 249.7$ Hz) ppm.

3.4. Preparation of the alkynyl complexes $[\text{M}(\text{C}\equiv\text{CR})(\text{CO})_2(\text{dppe})(\text{NO})]$

3.4.1. $\text{M} = \text{Mo}$ ($\text{R} = \text{H}$ (**2a**), ^iBu (**3a**), ^nPr (**4a**), ^iPr (**5a**), Ph (**6a**), CH_2OCH_3 (**7a**), SiMe_3 (**8a**))

To a suspension of *mer*- $[\text{Mo}(\text{CO})_3(\text{dppe})(\text{NO})][\text{BF}_4]$ (0.5 mmol) in THF (20 cm^3) was added at room temperature 0.5 mmol of $\text{LiC}\equiv\text{CR}$ (prepared in situ by treating the corresponding alkyne with 1.6 M Li^nBu in 15 cm^3 of THF at -20°C). The mixture was stirred at room temperature (ca. 2–3 h), filtered over Kieselguhr and evaporated to dryness giving a solid residue. The solid was dissolved in dichloromethane (2 cm^3) and transferred to an Alox IV chromatography column. Elution with hexane–dichloromethane (4:1) afforded the desired compounds after evaporation of the eluent. Complex **2a** was similarly prepared and purified using $\text{NaC}\equiv\text{CH}$ (18 wt.% slurry in xylene/light mineral oil). Yield (%); color; mass spectrum (m/e); IR (KBr, $\nu(\text{C}\equiv\text{C}) \text{ cm}^{-1}$); analytical and NMR spectroscopic data (^1H , $^{13}\text{C}\{^1\text{H}\}$) are as follows.

2a. 33; yellow; $[M^+-2CO] = 551$, $[M^+-2CO-NO-(C\equiv CH)] = 497$. Anal. Found: C, 57.8; H, 4.05; N, 2.4. $C_{30}H_{25}MoNO_3P_2$. Calc.: C, 59.5; H, 4.2; N, 2.3%. 1H RMN: δ 1.36 (t, 1H, $^4J(P-H) = 3.4$ Hz, $\equiv CH$), 2.43 (m, 2H, $P(CH_aH_b)_2P$), 2.94 (m, 2H, $P(CH_aH_b)_2P$), 7.24–7.78 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 27.15 (m, $P(CH_2)_2P$), 101.03 (s, C_β), 118.47 (t, $^2J(C-P) = 16.2$ Hz, C_α), 128–134.86 (Ph), 218 (dd, $^2J(C-P) = 42.6$, 10.6 Hz, 2 *cis* CO) ppm.

3a. 90; yellow; $[M^+-CO] = 607$, $[M^+-2CO-NO-(C\equiv C'Bu)] = 497$; 2069 vw. Anal. Found: C, 61.35; H, 4.9; N, 2.0. $C_{34}H_{33}MoNO_3P_2$. Calc.: C, 61.7; H, 5.0; N, 2.1%. 1H RMN: δ 0.66 (s, 9H, $C(CH_3)_3$), 2.50 (m, 2H, $P(CH_aH_b)_2P$), 2.93 (m, 2H, $P(CH_aH_b)_2P$), 7.41–7.91 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 27.01 (m, $P(CH_2)_2P$), 29.09 (s, $C(CH_3)_3$), 31.91 (s, $C(CH_3)_3$), 105.43 (t, $^2J(C-P) = 17.0$ Hz, C_α), 123.97 (s, C_β), 128.85–135.02 (Ph), 218.79 (dd, $^2J(C-P) = 44.6$, 10.9 Hz, 2 *cis* CO) ppm.

4a. 39; yellow; 2094 vw. Anal. Found: C, 61.5; H, 4.7; N, 2.0. $C_{33}H_{31}MoNO_3P_2$. Calc.: C, 61.2; H, 4.8; N, 2.2%. 1H RMN: δ 0.47 (t, 3H, $J(H-H) = 7.2$ Hz, CH_3), 0.83 (m, 2H, CH_2), 1.46 (m, 2H, $\equiv CCH_2$), 2.33 (m, 2H, $P(CH_aH_b)_2P$), 2.80 (m, 2H, $P(CH_aH_b)_2P$), 7.31–7.78 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 14.26 (s, CH_3), 23.45 (s, CH_2), 23.85 (s, $\equiv CCH_2$), 27.20 (m, $P(CH_2)_2P$), 109.28 (t, $^2J(C-P) = 16.3$ Hz, C_α), 115.54 (s, C_β), 128.66–135.32 (Ph), 218.54 (dd, $^2J(C-P) = 44.4$, 10.7 Hz, 2 *cis* CO) ppm.

5a. 43; yellow; $[M^+-2CO] = 597$, $[M^+-2CO-NO-(C\equiv CCHMe_2)] = 497$; 2075 vw. Anal. Found: C, 62.1; H, 4.8; N, 2.1. $C_{34}H_{31}MoNO_3P_2$. Calc.: C, 61.2; H, 4.8; N, 2.15%. 1H RMN: δ 0.55 (d, 6H, $J(H-H) = 6.8$ Hz, CH_3), 1.90 (m, 1H, $\equiv CCH$), 2.41 (m, 2H, $P(CH_aH_b)_2P$), 2.86 (m, 2H, $P(CH_aH_b)_2P$), 6.67–7.83 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 22.94 (s, $CH(CH_3)_2$), 24.05 (s, $CH(CH_3)_2$), 27.06 (m, $P(CH_2)_2P$), 107.42 (t, $^2J(C-P) = 16.9$ Hz, C_α), 121.42 (s, C_β), 128.73–134.99 (Ph), 218.65 (dd, $^2J(C-P) = 44.7$, 10.8 Hz, 2 *cis* CO) ppm.

6a. 34; yellow; $[M^+-2CO] = 627$, $[M^+-2CO-NO-(C\equiv CPh)] = 497$; 2075 vw. Anal. Found: C, 62.8; H, 4.3; N, 2.0. $C_{36}H_{29}MoNO_3P_2$. Calc.: C, 63.45; H, 4.3; N, 2.0%. 1H RMN: δ 2.41 (m, 2H, $P(CH_aH_b)_2P$), 2.90 (m, 2H, $P(CH_aH_b)_2P$), 6.54–7.75 (m, 25H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 27.12 (m, $P(CH_2)_2P$), 114.69 (s, C_β), 126.12–135.25 (C_α , Ph), 218.25 (dd, $^2J(C-P) = 43.3$, 10.9 Hz, 2 *cis* CO) ppm.

7a. 32; yellow; $[M^+-2CO] = 595$, $[M^+-2CO-NO-(C\equiv CCH_2OCH_3)] = 497$. Anal. Found: C, 57.05; H, 4.5; N, 2.2. $C_{32}H_{29}MoNO_3P_2$. Calc.: C, 59.2; H, 4.5; N, 2.1%. 1H RMN: δ 2.34 (m, 2H, $P(CH_aH_b)_2P$), 2.76 (s, 3H, OCH_3), 2.82 (m, 2H, $P(CH_aH_b)_2P$), 3.34 (t, 2H, $^5J(H-P) = 2.7$ Hz, $\equiv CCH_2$), 7.19–7.67 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 27.16 (m, $P(CH_2)_2P$), 56.96 (s, OCH_3), 61.81 (s, $\equiv CCH_2$), 110.01 (s, C_β), 119.24

(t, $^2J(C-P) = 16.8$ Hz, C_α), 128.78–135.17 (Ph), 218.31 (dd, $^2J(C-P) = 43.3$, 10.8 Hz, 2 *cis* CO) ppm.

8a. 43; yellow; $[M^+-2CO] = 623$, $[M^+-2CO-NO-(C\equiv CSiMe_3)] = 497$. Anal. Found: C, 57.8; H, 5.0; N, 2.1. $C_{33}H_{33}MoNO_3P_2Si$. Calc.: C, 58.5; H, 4.9; N, 2.1%. 1H RMN: δ -0.41 (s, 9H, $Si(CH_3)_3$), 2.40 (m, 2H, $P(CH_aH_b)_2P$), 2.81 (m, 2H, $P(CH_aH_b)_2P$), 7.18–7.71 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 0.38 (s, $Si(CH_3)_3$), 26.30 (m, $P(CH_2)_2P$), 121.57 (s, C_β), 128.12–133.97 (Ph), 147.23 (t, $^2J(C-P) = 16.0$ Hz, C_α), 217.70 (dd, $^2J(C-P) = 42.6$, 10.8 Hz, 2 *cis* CO) ppm.

3.4.2. $M = W$ ($R = H$ (2b), iBu (3b), nPr (4b))

To a suspension of *mer*- $[W(CO)_3(dppe)(NO)] [BF_4]$ (0.5 mmol) in THF (20 cm³) was added at room temperature 0.5 mmol of $LiC\equiv CR$ (prepared in situ by treating the corresponding alkyne with 1.6 M Li^nBu in 15 cm³ of THF at $-20^\circ C$). The mixture was heated under reflux for approximately 5 h, filtered over Kieselguhr and evaporated to dryness giving a solid residue. The solid was dissolved in dichloromethane (2 cm³) and transferred to an Alox IV chromatography column. Elution with hexane–dichloromethane (4:1) afforded the desired compounds after evaporation of the solvent. Complex 2b was similarly prepared and purified using $NaC\equiv CH$ (18 wt.% slurry in xylene/light mineral oil). Yield (%); color; mass spectrum (*m/e*); IR (KBr, $\nu(C\equiv C)$, cm⁻¹); analytical, conductivity (acetone, 20°C, $\Omega^{-1} cm^2 mol^{-1}$) and NMR spectroscopic data (1H , $^{13}C\{^1H\}$) are as follows.

2b. 40; yellow. Anal. Found: C, 49.9; H, 3.8; N, 1.6. $C_{30}H_{25}NO_3P_2W$. Calc.: C, 52.0; H, 3.6; N, 2.0%. 1H RMN: δ 1.19 (t, 1H, $^4J(P-H) = 3.4$ Hz, $\equiv CH$), 2.40 (m, 2H, $P(CH_aH_b)_2P$), 2.91 (m, 2H, $P(CH_aH_b)_2P$), 7.31–7.67 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 27.76 (m, $P(CH_2)_2P$), 100.99 (s, C_β), 114.84 (t, $^2J(C-P) = 13.7$ Hz, C_α), 128.13–132.84 (Ph), 211.00 (dd, $^2J(C-P) = 40.40$, 6.6 Hz, 2 *cis* CO) ppm.

3b. 39; yellow; 2069 vw. Anal. Found: C, 52.6; H, 5.1; N, 1.4. $C_{34}H_{33}NO_3P_2W$. Calc.: C, 54.5; H, 4.4; N, 1.9%. 1H RMN: δ 0.50 (s, 9H, $C(CH_3)_3$), 2.42 (m, 2H, $P(CH_aH_b)_2P$), 2.85 (m, 2H, $P(CH_aH_b)_2P$), 7.30–7.74 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 27.52 (m, $P(CH_2)_2P$), 28.37 (s, $C(CH_3)_3$), 31.09 (s, $C(CH_3)_3$), 103.01 (t, $^2J(C-P) = 14.3$ Hz, C_α), 124.04 (s, C_β), 127.34–133.67 (Ph), 211.51 (dd, $^2J(C-P) = 42.1$, 6.8 Hz, 2 *cis* CO) ppm.

4b. 42; yellow; 2097 vw. Anal. Found: C, 52.9; H, 4.0; N, 1.3. $C_{33}H_{31}NO_3P_2W$. Calc.: C, 53.9; H, 4.25; N, 1.9%. 1H RMN: δ 0.57 (t, 3H, $J(H-H) = 7.2$ Hz, CH_3), 0.93 (m, 2H, CH_2), 1.54 (m, 2H, $\equiv CCH_2$), 2.51 (m, 2H, $P(CH_aH_b)_2P$), 2.98 (m, 2H, $P(CH_aH_b)_2P$), 7.30–7.80 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ RMN: δ 13.48 (s, CH_3), 22.59 (s, CH_2), 23.06 (s, $\equiv CCH_2$), 27.73 (m, $P(CH_2)_2P$), 106.62 (t, $^2J(C-P) = 14.2$ Hz, C_α), 115.56

(s, C_β), 127.97–134.10 (Ph), 211.34 (dd, ²J(C–P) = 42.0, 6.4 Hz, 2 *cis* CO) ppm.

3.5. Preparation of the complexes [M(CO)₂(NCMe)(dppe)(NO)][BF₄] (M = Mo (9a), W (9b))

A solution of *mer*-[M(CO)₃(dppe)(NO)][BF₄] (0.5 mmol) in acetonitrile (25 cm³) was heated to 50°C for 2.5 h (M = Mo) or under reflux for 5 h (M = W). The solvent was evaporated under reduced pressure and the solid formed was washed with diethyl ether (3 × 10 cm³) and with hexane (3 × 10 cm³) and vacuum dried. Yield (%); color; IR (CH₂Cl₂, ν(C=O), ν(N=O), cm⁻¹); KBr, ν(C=N), ν(B–F), cm⁻¹); analytical, conductivity (acetone, 20°C, Ω⁻¹ cm² mol⁻¹) and NMR spectroscopic data are as follows.

9a. 92; orange; 2051 vs, 1988 vs, 1691 s; 2316 vw, 2283 vw, 1061 s, br. Anal. Found: C, 51.7; H, 3.9; N, 4.0. C₃₀H₂₃BF₄MoN₂O₃P₂. Calc.: C, 50.9; H, 3.9; N, 3.95%. 105, ¹H RMN: δ 1.64 (s, 3H, NCCH₃), 2.67 (m, 2H, P(CH₂H_b)₂P), 3.20 (m, 2H, P(CH₂H_b)₂P), 7.27–7.73 (m, 20H, Ph) ppm. ³¹P{¹H} RMN: δ 49.00 ppm. ¹³C{¹H} RMN: δ 1.98 (s, NCCH₃), 25.25 (m, P(CH₂)₂P), 126.98 (s, NCCH₃), 129.03–132.55 (Ph), 213.42 (dd, ²J(C–P) = 41.2, 9.8 Hz, 2 *cis* CO) ppm.

9b. 98; yellow; 2038 vs, 1967 vs, 1681 s; 2316 vw, 2282 vw, 1063 s, br. Anal. Found: C, 45.1; H, 3.5; N, 2.7. C₃₀H₂₃BF₄N₂O₃P₂W. Calc.: C, 45.3; H, 3.4; N, 3.5%. 120, ¹H RMN: δ 1.68 (s, 3H, NCCH₃), 2.67 (m, 2H, P(CH₂H_b)₂P), 3.30 (m, 2H, P(CH₂H_b)₂P), 7.45–7.56 (m, 20H, Ph) ppm. ³¹P{¹H} RMN: δ 41.31 (s, J(P–W) = 250.0 Hz) ppm. ¹³C{¹H} RMN: δ 2.14 (s, NCCH₃), 26.39 (m, P(CH₂)₂P), 126.37 (s, NCCH₃), 129.23–132.81 (Ph), 209.53 (dd, ²J(C–P) = 38.0, 9.8 Hz, 2 *cis* CO) ppm.

3.6. Preparation of the complex [Mo(CO)(NCMe)₂(dppe)(NO)][BF₄] (10a)

A solution of 9a (0.5 mmol) or 1b (0.5 mmol) in acetonitrile (35 cm³) was heated under reflux for 5 h. The solvent was evaporated under reduced pressure and the solid formed was washed with diethyl ether (3 × 10 cm³) and with hexane (3 × 10 cm³) and vacuum dried. Yield (%); color; IR (CH₂Cl₂, ν(C=O), ν(N=O), cm⁻¹); KBr, ν(C=N), ν(B–F), cm⁻¹); analytical data; conductivity (acetone, 20°C, Ω⁻¹ cm² mol⁻¹) and NMR spectroscopic data are as follows. 98; orange-red; 1957 vs, 1648 s; 2314 vw, 2282 vw, 1062 s, br. Anal. Found: C, 50.9; H, 4.2; N, 5.0. C₃₁H₂₆BF₄MoN₃O₂P₂. Calc.: C, 51.6; H, 4.2; N, 5.8%. 132, ¹H RMN: δ 1.57 (s, 3H, NCCH₃), 2.41 (s, 3H, NCCH₃), 2.34–2.84 (m, 4H, P(CH₂)₂P), 7.19–7.74 (m, 20H, Ph) ppm. ³¹P{¹H} RMN: δ 40.89 (d, ²J(P–P) + ³J(P–P) = 0.84 Hz, P_a(CH₂)₂P_b) 66.26 (d, ²J(P–P) + ³J(P–P) = 0.84 Hz, P_b(CH₂)₂P_a) ppm. ¹³C{¹H} RMN: δ 2.03 (s, NCCH₃), 4.01 (s, NCCH₃), 25.82 (m, PC₂H₂C₆H₂P), 26.74 (m,

PC₂H₂C₆H₂P), 125.05 (s, NCCH₃), 128.50 (s, NCCH₃), 128.88–134.89 (Ph), 226.37 (dd, ²J(C–P) = 48.9, 8.5 Hz, 2 *cis* CO) ppm.

3.7. Preparation of the complexes [M(CO)₂(dppe)(PR₃)(NO)][BF₄] (M = Mo; PR₃ = PMe₃ (11a), PMe₂Ph (12a). M = W; PR₃ = PMe₃ (11b), PMe₂Ph (12b))

A mixture of [M(CO)₂(NCMe)(dppe)(NO)][BF₄] (0.15 mmol) and the corresponding phosphine (0.15 mmol) in CH₂Cl₂ (10 cm³) was stirred at room temperature for 2 h (11a, 12a) or heated under reflux for 5 h (11b, 12b). The resulting solution was evaporated to dryness and the solid was washed with diethyl ether (3 × 5 cm³) and vacuum dried. Yield (%); color; IR (CH₂Cl₂, ν(C=O), ν(N=O), cm⁻¹); KBr, ν(B–F), cm⁻¹); analytical data; conductivity (acetone, 20°C, Ω⁻¹ cm² mol⁻¹) and NMR spectroscopic data are as follows.

11a. 75; yellow; 2037 vs, 1973 vs, 1700 s; 1061 s, br. Anal. Found: C, 49.3; H, 4.4; N, 1.8. C₃₁H₃₃BF₄MoNO₃P₂. Calc.: C, 49.3; H, 4.4; N, 1.8%. 123, ¹H RMN: δ 0.52 (d, 9H, ²J(H–P) = 7.8 Hz, P(CH₃)₃), 2.86 (m, 2H, P(CH₂CH₂)₂P), 3.34 (m, 2H, P(CH₂H_b)₂P), 7.45–7.85 (m, 20H, Ph) ppm. ³¹P{¹H} RMN: δ -36.07 (t, ²J(P–P) = 26.0 Hz, P(CH₃)₃), 45.46 (d, ²J(P–P) = 26.0 Hz, P(CH₂)₂) ppm. ¹³C{¹H} RMN: δ 15.08 (d, J(C–P) 25.3 Hz, P(CH₃)₃) 24.58 (m, P(CH₂)₂P), 128.95–132.77 (Ph), 216.08 (m, 2 *cis* CO) ppm.

12a. 87; yellow; 2038 vs, 1974 vs, 1700 s; 1058 s, br. Anal. Found: C, 54.5; H, 4.5; N, 1.8. C₃₆H₃₃BF₄MoNO₃P₂. Calc.: C, 53.7; H, 4.4; N, 1.7%. 123, ¹H RMN: δ 0.69 (d, 6H, ²J(H–P) = 7.5 Hz, P(CH₃)₂Ph), 2.84 (m, 2H, P(CH₂CH₂)₂P), 3.45 (m, 2H, P(CH₂H_b)₂P), 6.56–6.65 (m, 2H, Ph), 7.42–7.82 (m, 23H, Ph) ppm. ³¹P{¹H} RMN: δ -23.05 (t, ²J(P–P) = 24.9 Hz, P(CH₃)₂Ph), 45.23 (d, ²J(P–P) = 24.9 Hz, P(CH₂)₂) ppm. ¹³C{¹H} RMN: δ 12.47 (d, J(C–P) 23.6 Hz, P(CH₃)₂Ph), 24.80 (m, P(CH₂)₂P), 128.80–131.96 (Ph), 215.63 (m, 2 *cis* CO) ppm.

11b. 81; yellow; 2025 vs, 1954 vs, 1688 s, 1070s, br. Anal. Found: C, 45.4; H, 4.3; N, 1.6. C₃₁H₃₃BF₄MoNO₃P₂W. Calc.: C, 44.8; H, 4.0; N, 1.7%. 120, ¹H RMN: δ 0.64 (d, 9H, ²J(H–P) = 8.3 Hz, P(CH₃)₃), 2.91 (m, 2H, P(CH₂CH₂)₂P), 3.42 (m, 2H, P(CH₂H_b)₂P), 7.44–7.86 (m, 20H, Ph) ppm. ³¹P{¹H} RMN: δ -48.14 (t, ²J(P–P) = 21.1 Hz, J(P–W) = 245.3 Hz, P(CH₃)₃), 34.32 (d, ²J(P–P) = 21.1 Hz, J(P–W) = 159.8 Hz, P(CH₂)₂) ppm. ¹³C{¹H} RMN: δ 15.17 (d, J(C–P) = 28.7 Hz, P(CH₃)₃), 25.82 (m, P(CH₂)₂P), 128.75–132.04 (Ph), 209.93 (m, 2 *cis* CO) ppm.

12b. 84; yellow; 2026 vs, 1956 vs, 1689 s, 1062 s, br. Anal. Found: C, 47.8; H, 4.25; N, 1.7. C₃₆H₃₅BF₄NO₃P₂W. Calc.: C, 48.4 H, 3.95; N, 1.6%.

122. ^1H RMN: δ 0.77 (d, 6H, $^2J(\text{H-P}) = 8.0$ Hz, $\text{P}(\text{CH}_3)_2\text{Ph}$), 2.94 (m, 2H, $\text{P}(\text{CH}_a\text{CH}_b)_2\text{P}$), 3.51 (m, 2H, $\text{P}(\text{CH}_a\text{H}_b)_2\text{P}$), 6.55–6.63 (m, 2H, Ph), 7.28–7.86 (m, 23H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ RMN: δ -34.66 (t, $^2J(\text{P-P}) = 20.2$ Hz, $J(\text{P-W}) = 158.9$ Hz, $\text{P}(\text{CH}_3)_2\text{Ph}$), 34.61 (d, $^2J(\text{P-P}) = 20.2$ Hz, $J(\text{P-W}) = 244.1$ Hz, $\text{P}(\text{CH}_2)_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 12.66 (d, $J(\text{C-P}) = 27.6$ Hz, $\text{P}(\text{CH}_3)_2\text{Ph}$), 26.16 (m, $\text{P}(\text{CH}_2)_2\text{P}$), 128.90–132.04 (Ph), 207.78 (m, 2 *cis* CO) ppm.

3.8. Preparation of the complexes $[\text{Mo}(\text{CO})(\text{NCMe})(\text{dppe})(\text{PR}_3)(\text{NO})][\text{BF}_4]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$ (13a), PPh_3 (14a), $\text{P}(\text{OPh})_3$ (15a))

Procedure a. A mixture of $[\text{Mo}(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})][\text{BF}_4]$ (0.105 g, 0.15 mmol) and the corresponding phosphine or phosphite (0.15 mmol) in THF (10 cm^3) was heated under reflux (ca. 1–3 h) to give an orange solution. The resulting solution was evaporated to dryness and the solid residue was extracted with dichloromethane (ca. 5 cm^3). The addition of hexane to the partially evaporated dichloromethane solution yielded a solid which was washed with diethyl ether (3 \times 5 cm^3) and vacuum dried (yield 85–90%).

Procedure b. A mixture of $[\text{Mo}(\text{CO})(\text{NCMe})_2(\text{dppe})(\text{NO})][\text{BF}_4]$ (0.107 g, 0.15 mmol) and the corresponding phosphine or phosphite (0.15 mmol) in THF (10 cm^3) was heated under reflux (ca. 15 min). The resulting solution was evaporated to dryness and the solid was washed with diethyl ether (3 \times 5 cm^3) and vacuum dried (yield 90–96%).

The procedure used, as well as the color, IR (CH_2Cl_2 , $\nu(\text{C}=\text{O})$, $\nu(\text{N}=\text{O})$, cm^{-1} ; KBr, $\nu(\text{C}=\text{N})$, $\nu(\text{B}-\text{F})$, cm^{-1}); analytical data, conductivity (acetone, 20°C, $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) and NMR spectroscopic data are as follows.

13a. (a and b) yellow; 1953 vs, 1644 s; 2312 vw, 2277 vw, 1058 s,br. Anal. Found: C, 53.7; H, 4.8; N, 2.5. $\text{C}_{37}\text{H}_{38}\text{BF}_4\text{MoN}_2\text{O}_2\text{P}_3$. Calc.: C, 54.3; H, 4.7; N, 3.4%. 128. ^1H RMN: δ 1.43 (s, 3H, NCCH_3), 1.64 (dd, 6H, $^2J(\text{H-P}) = 14.5$ Hz, $^4J(\text{H-P}) = 7.6$ Hz, $\text{P}(\text{CH}_3)_2\text{Ph}$), 2.13 (m, 2H, $\text{P}(\text{CH}_a\text{H}_b)_2\text{P}$), 2.80 (m, 2H, $\text{P}(\text{CH}_a\text{H}_b)_2\text{P}$), 7.07–7.56 (m, 25H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 4.41 (dd, $^2J(\text{P-P}) = 106.6$ Hz, 24.8 Hz, $\text{P}(\text{CH}_3)_2\text{Ph}$), 44.00 (d, $^2J(\text{P-P}) = 24.8$ Hz, $\text{P}_a(\text{CH}_2)_2\text{P}_b$), 55.48 (d, $^2J(\text{P-P}) = 106.6$ Hz, $\text{P}_a(\text{CH}_2)_2\text{P}_b$) ppm. $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 1.64 (s, NCCH_3), 16.27 (d, $J(\text{C-P}) = 41.7$ Hz, $^3J(\text{C-P}) = 25.2$ Hz, $\text{P}(\text{CH}_3)_2\text{Ph}$), 24.80 (m, $\text{PC}_a\text{H}_2\text{C}_b\text{H}_2\text{P}$), 28.00 (m, $\text{PC}_a\text{H}_2\text{C}_b\text{H}_2\text{P}$), 126.25 (s, NCCH_3), 128.55–133.22 (Ph), 227.98 (m, CO) ppm.

14a. (a and b) yellow; 1958 vs, 1636 s; 2311 vw, 2277 vw, 1062 s,br. Anal. Found: C, 59.3 H, 4.8; N, 2.5. $\text{C}_{47}\text{H}_{42}\text{BF}_4\text{MoN}_2\text{O}_2\text{P}_3$. Calc.: C, 59.9; H, 4.5; N, 3.0%. 133. ^1H RMN: δ 1.25 (s, 3H, NCCH_3), 2.50–3.50 (m, 4H, $\text{P}(\text{CH}_2)_2\text{P}$), 6.66–7.82 (m, 35H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$

RMN: δ 43.42 (dd, $^2J(\text{P-P}) = 22.2$ Hz, $^2J(\text{P-P}) + ^3J(\text{P-P}) = 8.0$ Hz, $\text{P}_a(\text{CH}_2)_2\text{P}_b$), 43.53 (d, $^2J(\text{P-P}) = 114.2$ Hz, 22.2 Hz, PPh_3), 53.09 (dd, $^2J(\text{P-P}) = 114.2$ Hz, $^2J(\text{P-P}) + ^3J(\text{P-P}) = 8.0$ Hz, $\text{P}_a(\text{CH}_2)_2\text{P}_b$) ppm. $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 1.46 (s, NCCH_3), 24.62 (m, $\text{PC}_a\text{H}_2\text{C}_b\text{H}_2\text{P}$), 29.27 (m, $\text{PC}_a\text{H}_2\text{C}_b\text{H}_2\text{P}$), 126.03 (s, NCCH_3), 127.59–134.52 (Ph), 229.94 (m, CO) ppm.

15a (a and b) yellow; 1981 vs, 1667 s; 2311 vw, 2277 vw, 1065 s,br. Anal. Found: C, 56.4 H, 4.5; N, 2.9%. $\text{C}_{47}\text{H}_{42}\text{BF}_4\text{MoN}_2\text{O}_2\text{P}_3$. Calc.: C, 57.0; H, 4.3; N, 2.9%. 129. ^1H RMN: δ 1.18 (s, 3H, NCCH_3), 2.10–3.10 (m, 4H, $\text{P}(\text{CH}_2)_2\text{P}$), 6.77–7.71 (m, 35H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 45.42 (dd, $^2J(\text{P-P}) = 33.7$ Hz, $^3J(\text{P-P}) = 6.7$ Hz, $\text{P}_a(\text{CH}_2)_2\text{P}_b$), 52.47 (dd, $^2J(\text{P-P}) = 191.40$ Hz, $^3J(\text{P-P}) = 6.7$ Hz, $\text{P}_a(\text{CH}_2)_2\text{P}_b$), 151.18 (dd, $^2J(\text{P-P}) = 191.40$ Hz, 33.7 Hz, $\text{P}(\text{OPh})_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 1.74 (s, NCH_3), 24.81 (m, $\text{PC}_a\text{H}_2\text{C}_b\text{H}_2\text{P}$), 26.83 (m, $\text{PC}_a\text{H}_2\text{C}_b\text{H}_2\text{P}$), 126.80 (s, NCH_3), 119.64–150.97 (Ph), 222.29 (m, CO) ppm.

3.9. Preparation of the complex $[\text{Mo}\{\text{S}(\text{o-C}_6\text{H}_4\text{Me})\}_2(\text{CO})_2(\text{dppe})(\text{NO})]$ (16a)

To a solution of 0.3 mmol of $\text{NaS}(\text{o-C}_6\text{H}_4\text{Me})$ in THF (20 cm^3) (prepared in situ by treating $\text{HS}(\text{o-C}_6\text{H}_4\text{Me})$ with NaH) was added at -5°C $[\text{Mo}(\text{CO})_2(\text{NCMe})(\text{dppe})(\text{NO})]$ (0.3 mmol). The mixture was stirred during 5 min and evaporated to dryness giving a solid residue which was extracted with dichloromethane (20 cm^3). The solvent was evaporated under reduced pressure and the solid formed was washed with hexane (3 \times 10 cm^3) and vacuum dried. Yield (%):

Table 3
Experimental data for the X-ray diffraction studies of complex 4a

Formula	$\text{C}_{33}\text{H}_{31}\text{MoNO}_3\text{P}_2$
Molecular weight	647.50
Crystal system	monoclinic
Space group	$P2_1/n$
Radiation (λ (Å))	graphite-monochromated (Mo K α , 0.71073)
a (Å)	15.647(6)
b (Å)	18.034(5)
c (Å)	11.207(4)
β (°)	98.22(2)
V (Å ³)	3130(2)
Z	4
D_{calc} (g cm^{-3})	1.374
$F(000)$	1328
Crystal size (mm^3)	0.15 \times 0.21 \times 0.27
μ (Mo K α) (cm^{-1})	5.54
θ range (°)	3–27
Reflections measured	$\pm h, k, l$
Unique total data	6818
Unique observed data	3862 [$I > 2\sigma(I)$]
$R = \Sigma \Delta F / \Sigma F_o $	0.0312
$R_w = [\Sigma w(\Delta F)^2 / \Sigma w(F_o)^2]^{1/2}$	0.0388

color; IR (CH_2Cl_2 , $\nu(\text{C}=\text{O})$, $\nu(\text{N}=\text{O})$, cm^{-1}); analytical and NMR spectroscopic data are as follows.

16a. 91; yellow; 2027 vs, 1963 vs, 1634 s. Anal. Found: C, 59.2; H, 4.5; N, 1.8. $\text{C}_{35}\text{H}_{31}\text{MoNO}_3\text{P}_2\text{S}$. Calc.: C, 59.75; H, 4.4; N, 2.0%. ^1H RMN: δ 1.78 (s, 3H CH_3), 2.41 (m, 2H, $\text{P}(\text{CH}_2\text{CH}_2)_2\text{P}$), 2.90 (m, 2H, $\text{P}(\text{CH}_2\text{CH}_2)_2\text{P}$), 6.20–6.78 (4H, $\text{SC}_6\text{H}_4\text{CH}_3$), 7.31–7.63 (m, 2H, Ph), 20 ppm. $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 44.75 ppm. $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 21.67 (s, $\text{SC}_6\text{H}_4\text{Me}$), 25.29 (m, $\text{P}(\text{CH}_2)_2\text{P}$), 123.33–144.15 (Ph, $\text{SC}_6\text{H}_4\text{Me}$), 216.56 (dd, $^2J(\text{C}-\text{P}) = 48.6, 9.0$ Hz, 2 *cis* CO).

3.10. X-ray data collection, structure determination and refinement for $[\text{Mo}(\text{C}\equiv\text{C}^n\text{Pr})(\text{CO})_2(\text{dppe})(\text{NO})]$ (4a)

The crystallographic data are summarized in Table 3. Data were collected at room temperature (22°C) on a

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) defined as one-third of the trace of the orthogonalized U_{ij} tensor for the non-hydrogen atoms of complex 4a

Atom	x	y	z	U
Mo	2572.3(2)	2364.7(2)	204.6(3)	298(1)
P(1)	1703.1(5)	2350.0(5)	-1887.8(8)	323(3)
P(2)	1124.9(5)	1895.8(5)	692.3(8)	320(3)
O(1)	4064(2)	3306(2)	-709(3)	839(15)
O(2)	3280(2)	2719(2)	2933(3)	770(13)
O(3)	3626(2)	956(2)	277(3)	567(11)
N	3176(2)	1496(2)	230(2)	352(10)
C(1)	3544(3)	2954(2)	-386(4)	498(14)
C(2)	3033(2)	2582(2)	1952(4)	438(13)
C(3)	1973(2)	3457(2)	218(3)	394(12)
C(4)	1686(3)	4068(2)	263(4)	509(15)
C(5)	1363(4)	4832(3)	381(5)	875(24)
C(6)	1069(4)	4990(3)	1564(5)	983(26)
C(7)	820(4)	5799(4)	1671(6)	1266(33)
C(8)	564(2)	2377(2)	-1650(3)	392(12)
C(9)	413(2)	1770(2)	-754(3)	378(12)
C(10)	1692(2)	1539(2)	-2890(3)	349(12)
C(11)	2145(2)	898(2)	-2519(3)	418(13)
C(12)	2097(3)	289(2)	-3270(4)	516(15)
C(13)	1615(3)	306(3)	-4381(4)	591(17)
C(14)	1164(4)	939(3)	-4756(4)	712(20)
C(15)	1203(3)	1545(3)	-4019(4)	630(18)
C(16)	1827(2)	3113(2)	-2914(3)	383(12)
C(17)	2540(3)	3129(3)	-3512(4)	616(17)
C(18)	2660(3)	3691(3)	-4316(5)	703(20)
C(19)	2072(4)	4252(3)	-4522(4)	654(20)
C(20)	1373(4)	4257(3)	-3919(4)	652(19)
C(21)	1251(3)	3693(2)	-3125(4)	513(15)
C(22)	1000(2)	1000(2)	1431(3)	371(12)
C(23)	217(3)	796(3)	1786(4)	540(16)
C(24)	120(3)	119(3)	2306(4)	638(19)
C(25)	788(3)	-369(3)	2493(4)	572(17)
C(26)	1566(3)	-182(3)	2153(4)	657(19)
C(27)	1671(3)	504(2)	1629(4)	528(16)
C(28)	544(2)	2523(2)	1568(3)	406(13)
C(29)	-224(3)	2870(2)	1098(5)	564(17)
C(30)	-639(4)	3336(3)	1820(7)	775(25)
C(31)	-291(5)	3460(3)	3004(7)	889(28)
C(32)	463(5)	3116(3)	3469(5)	816(24)
C(33)	882(3)	2652(3)	2756(4)	576(16)

Philips PW 1100 diffractometer using graphite-monochromated Mo K α radiation and $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min $^{-1}$ and a scan width from $(\theta - 0.65)^\circ$ to $(\theta + 0.65 + 0.346 \tan \theta)^\circ$. One standard reflection was monitored every 100 measurements; no significant decays was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen [22]. Intensities were corrected for Lorentz and polarization effects; no correction for absorption was necessary. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms (excepting those of the isopropyl groups which were placed at their geometrically calculated positions and refined riding the corresponding carbon atoms) were clearly localized in the final ΔF map and refined isotropically. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the K and g values were 0.768 and 0.0010 respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from Ref. [23]. All calculations were carried out on the GOULD POWERNODE 6040 of the "Centro di Studio per la Strutturistica Diffraattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [24]. The final atomic coordinates for the non-hydrogen atoms are given in Table 4. Additional data (atomic coordinates of the hydrogen atoms, atomic thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre or are available from the authors on request.

Acknowledgements

This work was supported by the Dirección General de Investigación Científica y Técnica (Project PB 93-0325). We thank the Ministerio de Educación y Ciencia for a fellowship grant (to L.Z.).

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