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Reaction of metal carbonyl anions with electrophilic alkynes: Synthesis of isomeric η^3-acryloyl and σ-vinyl complexes

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Abstract

Treatment of the metal carbonylate anions $[CpMo(CO)_2(L)]^-$ ($Cp = \eta$-C_5H_5; $L = PPh_2Me$, PPh_2Et) with the electrophilic alkynes methyl propiolate or DMAD ($RC{\equiv}CCO_2Me$, where $R = H$ or CO_2Me, respectively) followed by protonation affords the η^3-acryloyl (1-oxoallyl) complexes $[CpMo(\eta^3\text{-}COCR{=}CHCO_2Me)(CO)(L)]$ (**3a–d**) as the major products, together with the isomeric vinyl complexes *trans*-$[CpMo(CR{=}CHCO_2Me)(CO)_2(L)]$ (**4a–d**). On the basis of the regioselectivity of the reaction, it is proposed that nucleophilic attack of the carbonylate anion occurs at the alkyne carbon bearing R; migration of the anionic vinyl ligand to a CO followed by protonation gives **3**, whereas protonation without insertion gives **4**. The X-ray structures of the acryloyl complex $[CpMo(\eta^3\text{-}COCH{=}CHCO_2Me)(CO)(PPh_2Me)]$ (**3b**) and its vinyl isomer $[CpMo(\sigma\text{-}CH{=}CHCO_2Me)(CO)_2(PPh_2Me)]$ (**4b**) have been determined.

Keywords: Molybdenum; Phosphine; Acryloyl; Vinyl; Migratory insertion

1. Introduction

The formation of a carbon–carbon bond between a coordinated organic fragment and a carbonyl ligand by migratory insertion is one of the cornerstones of organometallic chemistry, and forms a key step in many industrial processes [1]. Because (at least in part) of the increased metal–carbon bond strength, migratory insertion reactions involving M–C(sp^2) or M–C(sp) bonds are less common than those of simple alkyl groups and consequently examples of the insertion of CO into metal-vinyl or metal-acetylide bonds are comparatively rare. As a result the chemistry of complexes containing the acryloyl (vinylacyl) ligand (η^1- or η^3-$COCH{=}CH_2$) remains relatively unexplored.

The nucleophilic properties of metal carbonyl anions make them an invaluable synthetic tool for the organometallic chemist, allowing access to alkyl and acyl complexes through reaction with organic halides, and to compounds with metal–element bonds by reaction with main group or transition metal halides. A series of papers by Beck and co-workers described the attack of metal carbonyl anions on (usually cationic) complexes with π-bound ligands such as alkenes, alkynes and arenes, leading in favourable cases to hydrocarbon-bridged species [2]. In contrast, the reactions of metal carbonyl anions with uncomplexed alkynes appear to be limited to only a few examples. For example, Mitsudo and co-workers showed that $[PPN][FeH(CO)_4]$ reacted with activated alkynes $RC{\equiv}CCO_2Me$ ($R = H$, CO_2Me) to give the acryloyl complexes $[PPN][Fe\{COC(CO_2Me){=}CHR\}(CO)_3]$ by insertion of the alkyne into the metal–hydride bond followed by vinyl to carbonyl migration [3]. Wojcicki has reported that $Na[Re(CO)_5]$ reacts with $RC{\equiv}CCO_2Me$ ($R = H$, Me, CO_2Me) to give initially anionic metallacyclobutenones,

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which can be alkylated at oxygen to give rhenacyclobutadienes [4]. Most relevantly Lee et al. have found that the reaction of $[CpM(CO)_3]^-$ (M = Mo, W) with HC≡CCOMe in a THF/MeOH/H_2O solvent mixture afforded initially the vinyl complexes $[CpM(CO)_3(CH{=}CHCOMe)]$ which then underwent carbonylation to the cyclic lactone $[CpM(CO)_2\{\eta^3\text{-}CHCHC(Me)OCO\}]$; an η^3-acryloyl complex was implicated in this process but not isolated [5].

We have previously reported that the anion $[CpMo(CO)_2(PPh_2COMe)]^-$, prepared by deprotonation of $[CpMo(CO)_2(PPh_2H)(COMe)]$ at room temperature (which induces a migration of the acyl group from molybdenum to phosphorus) reacts with RC≡CCO_2Me (R = H, CO_2Me) to give the acryloyl complexes $[CpMo(CO)(PPh_2COMe)(\eta^3\text{-}COCR{=}CHCO_2Me)]$ together with much lower yields of associated vinyl complexes [6]. We therefore sought to establish whether this was a general reaction of substituted carbonyl anions of the type $[CpMo(CO)_2(L)]^-$ with tertiary phosphine ligands, and in this paper we report our results which show that this is indeed the case.

2. Results and discussion

2.1. Anion synthesis

The substituted carbonyl anions $[CpMo(CO)_2(L)]^-$ **1a** (L = PPh_2Me) and **1b** (L = PPh_2Et) were conveniently prepared in THF solution in one of two ways. The first method was that used previously by us, involving cleavage of the corresponding substituted dimers $[Cp_2Mo_2(CO)_4L_2]$ with sodium amalgam; these dimers were prepared in *ca.* 75% yield by addition of two equiv. of L to $[Cp_2Mo_2(CO)_4]$, made *in situ* from $[Cp_2Mo_2(CO)_6]$ [7,8]. However an alternative route was also used in this work, in which $[Cp_2Mo_2(CO)_6]$ was first cleaved with iodine to give $[CpMo(CO)_3I]$, followed by substitution with L in the presence of Me_3NO to give $[CpMo(CO)_2(L)I]$ **2a**, **2b**. Although **2a** has been previously mentioned in a paper and a patent [9], no preparative details or characterising data have previously been published for either of these compounds; therefore we include them in Section 5. Sodium amalgam reduction of these iodide complexes provided the requisite anions. The advantages of this second route are that both of the reactions to prepare $[CpMo(CO)_2(L)I]$ are rapid, in contrast to the overnight reflux required for the generation of $[Cp_2Mo_2(CO)_4]$, and secondly the generation of the anion is also more rapid, probably due to the greater solubility of the phosphine iodide complexes compared to the dimers. The overall yield of both methods is comparable.

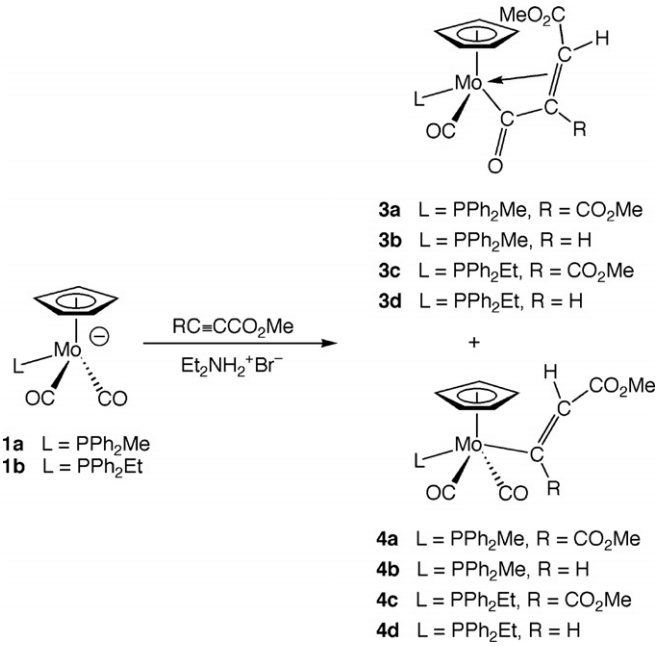
In this paper, we restrict ourselves to discussion of the complexes with L = PPh_2Me and PPh_2Et, but in principle L can be any tertiary phosphine ligand. We have shown that the reaction below also works for L = PPh_3 and P^nBu_3; however in the former case the relative insolubility of $[Cp_2Mo_2(CO)_4(PPh_3)_2]$ resulted in lower yields, and in the latter case oily products were formed which could not be isolated as analytically pure materials.

2.2. Reaction with activated alkynes

Addition of a slight excess of the activated alkyne to solutions of anions **1a** or **1b** causes an immediate darkening in colour in the case of DMAD, and a somewhat slower reaction (about 10 min) for methyl propiolate. In each case protonation with a weak acid (in this work $[Et_2NH_2][Br]$ was routinely used as it was found to give the cleanest reaction) yielded two products that could be separated by column chromatography (Scheme 1). The lowest yields of both products were found in the reaction of the least nucleophilic anion (L = PPh_2Me) with the least electrophilic alkyne (methyl propiolate).

The major products were the η^3-acryloyl complexes $[CpMo(\eta^3\text{-}COCR{=}CHCO_2Me)(CO)(L)]$ (**3a**–**d**), produced in *ca.* 50% yield as orange, air-stable crystalline solids displaying a single strong terminal ν(CO) peak in their IR spectra, together with weaker peaks due to the acryloyl carbonyl and the ester groups. Their ^{1}H NMR spectra are unremarkable but in the case of the complexes derived from methyl propiolate, show that the carbonyl group of the acryloyl ligand is joined to the CH terminus of the alkyne, and the magnitude of the *J*(HH) coupling constant indicates that the two protons of the acryloyl ligand are in a *cis* conformation. The distinguishing feature in the spectroscopic data of **3** is the peak at approximately 250 ppm in the ^{13}C NMR spectrum due to the carbonyl of the η^3-acryloyl unit; this carbon atom also shows coupling to the ^{31}P nucleus of the phosphine whereas the other two acryloyl carbons, which occur at unusually low chemical shifts (25–45 ppm) do not.

A number of related acryloyl complexes of Group 6 metals are known. While this work was in progress, Lin



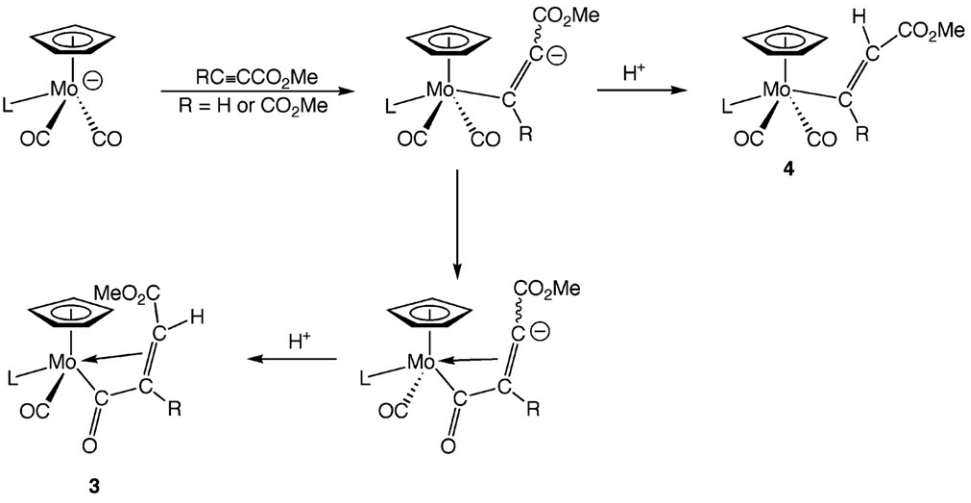
Scheme 1. Synthesis of the η^3-acryloyl and σ-vinyl complexes.

and co-workers reported a similar reaction between Li[CpMo(CO)$_2$(PPh$_3$)] (prepared in this instance from [CpMo(CO)$_2$(PPh$_3$)I] by treatment with BuLi) and methyl propiolate to afford the analogous acryloyl complex [CpMo (η^3-COCH=CHCO$_2$Me)(CO)(PPh$_3$)] [5]. The unsubstituted acryloyl [CpMo(η^3-COCH=CH$_2$)(CO)(PPh$_3$)] was prepared by decomposition of the alkyl complex [CpMo{CHMe(OMe)}(CO)$_2$(PPh$_3$)] with loss of MeOH, a reaction which also involves vinyl-to-carbonyl migration [10]. Similar treatment of the tungsten analogue produced exclusively the isomeric vinyl complex [CpW(σ-CH=CH$_2$)(CO)$_2$(PPh$_3$)] instead. Some years ago, Guerchais and co-workers reported that the photochemical reaction of [CpM(CO)$_3$H] (M = Mo, W) with hexafluoro-but-2-yne produced the acryloyl complexes [CpM(CO)$_2${η^3-COC(CF$_3$)=CHCF$_3$}], which could be converted into their σ-vinyl isomers [CpM(CO)$_3${σ-C(CF$_3$)=CHCF$_3$}] by heating; photolysis reversed this transformation [11]. Reaction of the tungsten acryloyl complex with phosphine ligands afforded [CpW(CO)(L){COC(CF$_3$)=CHCF$_3$}] (L = PPh$_3$, P(OMe)$_3$, PMe$_3$, PMe$_2$Ph), with the organic ligand remaining intact; these substituted acryloyls could also be interconverted with their vinyl isomers [CpW(CO)$_2$(L){σ-C(CF$_3$)=CHCF$_3$}]. Similar acryloyl complexes were prepared by Brix and Beck from the alkyne HC≡CNEt$_2$ [12]. However photochemical reactions of [CpM(CO)$_3$R] (R = H, alkyl) with other alkynes R^{1}C≡CR^2 are known to lead to cyclic alkenylketone complexes of the type [CpM(CO)$_2$(CR^1=CR^{2}CR=O)], which have been studied in detail by Alt [13].

The minor product of each reaction was the corresponding vinyl complex *trans*-[CpMo(σ-CR=CHCO$_2$Me)(CO)$_2$(L)] (**4a**–**d**), *i.e.* the isomers of **3a**–**d**. Their IR spectra show the two-peak pattern typical of a *trans* dicarbonyl geometry. Those derived from methyl propiolate show a low-field signal due to the α-CH proton in their ^{1}H NMR spectra (coupled to the other vinylic proton and the phosphine ligand) and demonstrating that the reaction is again regioselective. The magnitude of the J(HH) coupling constants in these two compounds (16.8 Hz in **4b**, 16.5 Hz in **4d**) indicates a *trans*-disposition of the two hydrogens across the vinylic double bond, as opposed to the *cis* arrangement seen in **3**. In the ^{13}C NMR spectra, the α-carbon of the vinyl group appears at approximately 180 ppm, with the β-carbon at approximately 130 ppm (in some cases the latter is hidden by the phenyl resonances). In the ^{31}P NMR spectra, it is noticeable that the signals for the vinyl complexes appear at higher chemical shift than those of the isomeric acryloyls, with the difference being approximately 20 ppm for L = PPh$_2$Me and about 10 ppm for L = PPh$_2$Et.

The proposed mechanism for the reaction is shown in Scheme 2. Initial nucleophilic attack of the carbonylate anion occurs regioselectively at the alkyne terminus which bears the R group; protonation of this anionic intermediate produces the vinyl complexes **4**. However it can also undergo a migratory insertion to give a σ-COCR=CCO$_2$Me$^-$ group, which on protonation forms the η^3-COCR=CHCO$_2$Me ligand in complexes **3**. Since vinyl complexes **4** are stable and do not rearrange to **3** at room temperature, the migration reaction must occur while the ligand is still in the anionic state. In order to explain the observed stereochemistry, the migration reaction of the intermediate in which the R and CO$_2$Me groups are situated *trans* to each other, leading to the acryloyl, would have to be faster than that of the intermediate in which they are *cis* to each other. It is not immediately obvious why this should be so, though one possibility might be the temporary coordination of a CO$_2$Me lone pair to the metal which might assist the CO migration.

However we can also not rule out a mechanism in which CO insertion occurs in all cases to give an acryloyl ligand, but on protonation only those molecules which have a *cis*-arrangement of the two original alkyne substituents (*i.e.* in the case of methyl propiolate, a *trans*-arrangement of the two hydrogens) undergo a subsequent de-insertion to give



Scheme 2. Proposed mechanism of the reaction.

the vinyl complex. This would also explain the differing stereochemistries of the two products. Careful examination of the chemical shifts of the other reported complexes of this type [11] suggests that the disubstituted acryloyl complexes (containing COCR=CHR groups) all share the same stereochemistry in which the R groups are *trans* to each other, and inspection of the structure of **3b** below suggests that having the substituent on the terminal carbon pointing down towards the phosphine ligand might be sterically unfavourable.

It is notable that the regiochemistry of the linking of the CO and alkyne ligands is different to that observed by Mitsudo [3] and Wojcicki [4]. In these cases, the CCO_2Me-terminus of methyl propiolate becomes attached to the CO; in the latter case this was explained by a mechanism involving nucleophilic attack of this β-carbon on the carbonyl ligand. In our work it is the CH-terminus which becomes linked to the CO; assuming that the initial nucleophilic attack is regiospecific (as we would expect from previous work, and from the regiochemistry of **4**) this implies a migratory insertion of CO into the metal-α-C bond. The synthesis of the unsubstituted acryloyl [$CpMo(\eta^3$-$COCH{=}CH_2)(CO)(PPh_3)$] was proposed to occur by a similar vinyl to CO migration [10].

As mentioned above, Lin and co-workers also explored the reaction of the unsubstituted anion $[CpW(CO)_3]^-$ with methyl propiolate and DMAD, and discovered that it gave exclusively the vinyl complexes [$CpW(CO)_3(\sigma$-$CR{=}CHCO_2Me)$] (R = H, CO_2Me) [5]. When we treated $[CpMo(CO)_3]^-$ with DMAD in a similar manner, an immediate reaction of the two compounds occurred, but on addition of H^+, the only isolated product was $[Cp_2Mo_2(CO)_6]$. It appears that the σ-vinyl complexes of tungsten may be rather more stable than those of molybdenum.

3. Crystal structure determinations

The crystal structure of [$CpMo(\eta^3$-$COCH{=}CHCO_2Me)(CO)(PPh_2Me)$] (**3b**) has been determined and is shown in Fig. 1, with selected bond lengths and angles collected in Table 1. The bond lengths within the $CpMo(CO)(PPh_2Me)$ unit all lie within the usual ranges and require little comment. In the η^3-acryloyl ligand, the carbonyl carbon is situated *trans* to the phosphine ligand (in keeping with the observation of ^{31}P coupling to this carbon in the ^{13}C NMR spectrum) and forms the shortest bond to the molybdenum atom [Mo(1)–C(7) 2.106(6) Å], whereas the other two carbons are equidistant [Mo(1)–C(8) 2.291(6) Å; Mo(1)–C(9) 2.304(6) Å]. The corresponding distances in the unsubstituted complex [$CpMo(\eta^3$-$COCH{=}CH_2)(CO)(PPh_3)$] were 2.105(28), 2.339(28) and 2.349(28) Å [10]. The carbon–carbon distances in the acryloyl ligand of **3b** are of equal length [C(7)–C(8), 1.448(9) Å and C(8)–C(9), 1.435(9) Å], emphasising the validity of the alternative 1-oxoallyl bonding description.

We also carried out a crystal structure determination of the isomeric vinyl complex *trans*-[$CpMo(\sigma$-$CH{=}CHCO_2Me)(CO)_2(PPh_2Me)$] (**4b**), shown in Fig. 2 with details given in Table 2. The *trans* orientation of the two carbonyl ligands and the *trans* arrangement of the two vinylic hydrogens were both confirmed. The Mo(1)–C(21) bond length of 2.173(6) Å and the C(21)–C(22) bond length of 1.325(10) Å are both comparable to the corresponding distances in other structurally characterised molybdenum vinyl species such as [$CpMo(\sigma$-$CH{=}CH^tBu)\{P(OMe)_3\}_3$] and [$CpMo(\sigma,\eta^2$-$CPh{=}CPhCH_2CH{=}CH_2)\{P(OMe)_3\}_2$] [14]. The vinylic bond length is longer than the average C=C bond length of 1.26 Å observed in the two indepen-

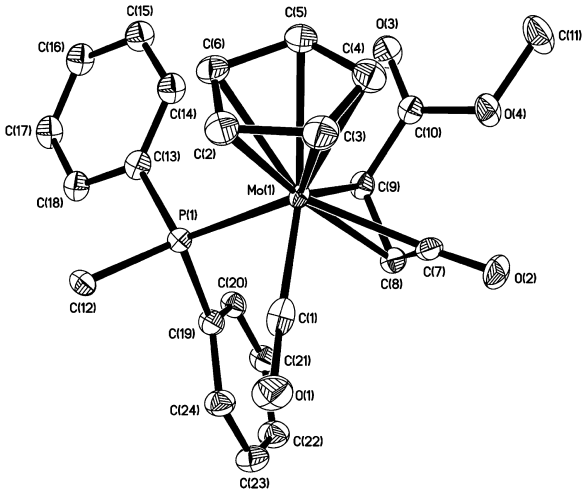


Fig. 1. Molecular structure of complex **3b** in the crystal (50% probability ellipsoids).

Table 1
Selected bond lengths (Å) and angles (°) for complex **3b**

Mo(1)–C(1)	1.944(8)	Mo(1)–C(7)	2.106(6)
Mo(1)–C(8)	2.291(6)	Mo(1)–C(9)	2.304(6)
Mo(1)–P(1)	2.5002(19)	O(1)–C(1)	1.178(8)
O(2)–C(7)	1.206(8)	C(7)–C(8)	1.448(9)
C(8)–C(9)	1.435(9)		
C(1)–Mo(1)–C(7)	78.4(3)	C(1)–Mo(1)–C(8)	86.1(2)
C(7)–Mo(1)–C(8)	38.2(2)	C(1)–Mo(1)–C(9)	118.9(2)
C(7)–Mo(1)–C(9)	66.0(2)	C(8)–Mo(1)–C(9)	36.4(2)
C(1)–Mo(1)–P(1)	82.7(2)	C(7)–Mo(1)–P(1)	125.40(19)
C(8)–Mo(1)–P(1)	90.21(18)	C(9)–Mo(1)–P(1)	80.17(18)
C(9)–C(8)–C(7)	113.3(6)		

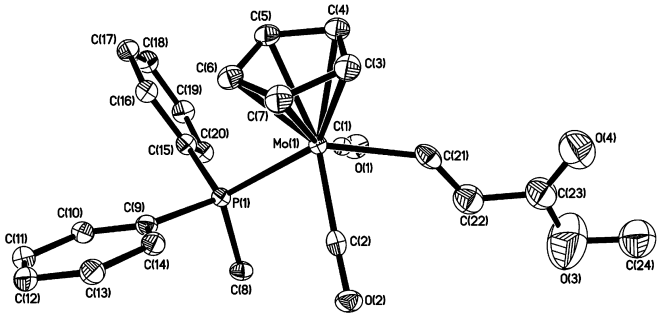


Fig. 2. Molecular structure of complex **4b** in the crystal (50% probability ellipsoids).

Table 2
Selected bond lengths (Å) and angles (°) for complex **4b**

Mo(1)–C(1)	1.963(6)	Mo(1)–C(2)	1.977(6)
Mo(1)–C(21)	2.173(6)	Mo(1)–P(1)	2.4677(14)
O(1)–C(1)	1.157(7)	O(2)–C(2)	1.152(7)
C(21)–C(22)	1.325(10)		
C(1)–Mo(1)–C(2)	99.8(2)	C(1)–Mo(1)–C(21)	72.6(2)
C(2)–Mo(1)–C(21)	74.5(2)	C(1)–Mo(1)–P(1)	76.70(16)
C(2)–Mo(1)–P(1)	80.57(16)	C(21)–Mo(1)–P(1)	135.97(17)
O(1)–C(1)–Mo(1)	178.9(5)	O(2)–C(2)–Mo(1)	177.7(5)
C(22)–C(21)–Mo(1)	135.9(5)		

dent molecules of $[(\eta\text{-}C_5H_4Me)W(\sigma\text{-}CH{=}CH_2)(CO)_2(PPh_3)]$, though the e.s.d.'s in this structure were relatively large [10].

4. Conclusions

The reaction of the substituted anions $[CpMo(CO)_2(L)]^-$ with the activated alkynes $RC{\equiv}CCO_2Me$ provides a general and regioselective route to η^3-acryloyl complexes $[CpMo(\eta^3\text{-}COCR{=}CHCO_2Me)(CO)(L)]$ when L is a phosphine ligand, through a process involving vinyl to carbonyl migration.

5. Experimental

General experimental techniques were as detailed in previous papers from this laboratory [15]. Infra-red spectra were recorded in CH_2Cl_2 solution on a Perkin–Elmer 1600 FT-IR machine using 0.5 mm NaCl cells. The ^1H, ^{13}C and ^{31}P NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 Fourier transform machine with automated sample-changer or on Bruker AMX400 or DRX-500 spectrometers. Chemical shifts are given on the δ scale relative to $SiMe_4 = 0.0$ ppm for ^1H and ^{13}C, and relative to 85% H_3PO_4 for ^{31}P. The $^{13}C\{^1H\}$ NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Kratos MS 80 instrument operating in either electron impact mode or fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix; the figures reported are the highest intensity peak of each isotope envelope. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry. The complexes $[Cp_2Mo_2(CO)_6]$ [16] and $[Cp_2Mo_2(CO)_4(L)_2]$ [8] were prepared by the literature methods. The iodide compound $[CpMo(CO)_3I]$ was prepared by treatment of a CH_2Cl_2 solution of $[Cp_2Mo_2(CO)_6]$ with a solution of one equivalent of I_2 dissolved in the same solvent [17]. Commercial $Me_3NO \cdot 2H_2O$ was rendered anhydrous by azeotropic distillation in toluene and stored under nitrogen.

5.1. Synthesis of $[CpMo(CO)_2(L)I]$ (**2a**, **2b**)

The complex $[CpMo(CO)_3I]$ (339.4 mg, 0.912 mmol) was dissolved in dichloromethane (15 cm^3) and one equivalent of PPh_2Me (0.17 cm^3, 0.912 mmol) was added, followed by a slight excess of anhydrous Me_3NO (80.4 mg, 1.07 mmol). After stirring for 90 min, no starting material remained as shown by the IR spectrum of an aliquot of the solution; the solvent was removed. Column chromatography of the residue produced a single red band, eluted with dichloromethane-light petroleum (2:3), which yielded an orange-red powder of $[CpMo(CO)_2(PPh_2Me)I]$ (453.7 mg, 91%). The compound exists as a mixture of *trans* and *cis* isomers in a ratio of 2:1 [18].

In a similar reaction, $[CpMo(CO)_3I]$ (503.3 mg, 1.353 mmol) reacted with PPh_2Et (0.28 cm^3, 1.353 mmol) in the presence of Me_3NO (112.3 mg, 1.497 mmol) to give $[CpMo(CO)_2(PPh_2Et)I]$ (577.8 mg, 76%). The compound exists as a mixture of *trans* and *cis* isomers in a ratio of 7:3.

Data for $[CpMo(CO)_2(PPh_2Me)I]$ (**2a**): IR: ν(CO) 1963s, 1879s cm^{-1}. *trans*-Isomer ^1H NMR: δ 7.50–7.35 (m, 10 H, Ph), 5.24 (s, 5 H, Cp), 2.50 (d, J 8.2 Hz, 3 H, Me); ^{13}C NMR: δ 232.4 (d, J_{PC} 26 Hz, CO), 136.4 (d, J_{PC} 46 Hz, C_{ipso}), 134.2–127.8 (m, Ph), 93.4 (s, Cp), 21.8 (d, J_{PC} 31 Hz, Me); ^{31}P NMR 27.0 ppm. *cis*-Isomer ^1H NMR δ 7.50–7.35 (m, 10H, Ph), 5.02 (d, J 1.9 Hz, 5H, Cp), 2.24 (d, J 8.6 Hz, 3H, Me); ^{13}C NMR δ 250.8 (d, J_{PC} 30.1 Hz, CO), 238.2 (d, J_{PC} 5.7 Hz, CO), 138.6 (d, J_{PC} 45.5 Hz, C_{ipso}), 134.2–127.8 (m, Ph), 93.5 (s, Cp), 21.8 (d, J_{PC} 31.4, Me); ^{31}P NMR: 46.3 ppm. Mass spectrum: m/z 544 (M^+), 516 ($M{-}CO)^+$. Anal. Calc. for $C_{20}H_{18}IMoO_2P$: C, 44.12; H, 3.31; I, 23.35. Found: C, 44.93; H, 3.08, I, 23.54%.

Data for $[CpMo(CO)_2(PPh_2Et)I]$ (**2b**): IR: ν(CO) 1963s, 1879s cm^{-1}. *trans*-Isomer ^1H NMR δ 7.62–7.35 (m, 10H, Ph), 5.26 (s, 5H, Cp), 2.65 (dq, J_{PH} 7.4, J_{HH} 7.4 Hz, 2H, CH_2), 1.15 (dt, J_{PH} 16.2 Hz, J_{HH} 7.4 Hz, 3H, Me); ^{13}C NMR: δ 233.2 (d, J_{PC} 27 Hz, CO), 136.0 (d, J_{PC} 41 Hz, C_{ipso}), 134.4–127.8 (m, Ph), 93.2 (s, Cp), 26.8 (d, J_{PC} 28 Hz, CH_2), 10.4 (J_{PC} 3 Hz, Me); ^{31}P NMR 38.5 ppm. *cis*-Isomer ^1H NMR δ 7.62–7.35 (m, 10H, Ph), 4.97 (d, J 1.8 Hz, 5H, Cp), 2.94 (dq, J_{PH} 7.6 Hz, J_{HH} 7.6 Hz, 2H, CH_2), 1.16 (m, 3H, Me); ^{13}C NMR: δ 251.4 (d, J_{PC} 29 Hz, CO), 238.4 (d, J_{PC} 5 Hz, CO), 134.6 (d, $J_{PC} = 42$ Hz, C_{ipso}), 134.4–127.8 (m, Ph), 93.5 (s, Cp), 27.1 (d, J_{PC} 33 Hz, CH_2), 9.0 (d, J_{PC} 3 Hz, Me); ^{31}P NMR 57.0 ppm. Mass spectrum m/z 558 (M^+), 530, 502 ($M{-}n$CO)$^+$, $n = 1$, 2. Anal. Calc. for $C_{21}H_{20}IMoO_2P$: C, 45.16; H, 3.58; I, 22.76. Found: C, 45.17; H, 3.45; I, 22.72%.

5.2. Synthesis of $[CpMo\{\eta^3\text{-}COC(CO_2Me){=}CHCO_2Me\}(CO)(PPh_2Me)]$ (**3a**) and $[CpMo(CO)_2\{C(CO_2Me){=}CHCO_2Me\}(PPh_2Me)]$ (**4a**)

A solution of the sodium salt of the anion $[CpMo(CO)_2(PPh_2Me)]^-$ was generated by stirring $[Cp_2Mo_2(CO)_4(PPh_2Me)_2]$ (500 mg, 0.60 mmol) in THF (40 cm^3) with an excess of sodium amalgam (0.3 g, 13.0 mmol Na in 5 cm^3 Hg). The solution was shaken until the initially sparingly soluble purple powder had

completely dissolved to give an olive green solution which was transferred to a second Schlenk tube by syringe. Addition of two molar equivalents of DMAD (0.16 cm^3, 1.30 mmol) caused an instantaneous colour change to orange-brown which darkened further on stirring for 10 min. The solution was then treated with $[Et_2NH_2][Br]$ (190 mg, 1.23 mmol), which produced no visible change, and then stirred for a further 25 min before removal of the solvent *in vacuo*. The resulting brown oily residue was then dissolved in the minimum volume of CH_2Cl_2 and loaded onto a silica column. Elution with light petroleum-CH_2Cl_2 (1:1) yielded 60 mg of the starting material $[CpMo(CO)_2(PPh_2Me)]_2$ (12% recovery). An orange band was removed using CH_2Cl_2–acetone (99:1) which gave a yellow powdery solid (90 mg, 13%), identified as vinyl complex **4a**. Further elution using a 9:1 mixture of the same solvents led to the isolation of acryloyl complex **3a** as a bright orange powder (310 mg, 46%).

In a similar reaction an anion solution prepared by the reduction of $[CpMo(CO)_2(PPh_2Me)I]$ (189.6 mg, 0.349 mmol) in 40 ml freshly distilled THF with sodium amalgam (0.30 g, 13.0 mmol sodium in 5 cm^3 mercury) was treated with DMAD (0.04 cm^3, 0.349 mmol) followed by diethylammonium bromide (59.8 mg, 0.388 mmol). The yields of products after chromatography were **4a**, 35.2 mg (18.1%) and **3a**, 117.4 mg (60.2%).

Data for **3a**: IR: ν(CO) 1949s, 1744sh, 1728m, 1691m cm^{-1}. ^1H NMR: δ 7.88–7.17 (m, 10H, Ph); 4.70 (s, 5H, Cp); 3.66 (d, J_{PH} 11.9, 1H, CH); 3.65 (s, 3H, CO_2Me); 3.64 (s, 3H, CO_2Me); 1.80 (d, J_{PH} 7.3, 3H, PMe). ^{13}C NMR: δ 251.5 (d, *J* 6, acyl CO); 236.0 (d, *J* 14, CO); 177.2 (s, *C*O_2Me); 173.0 (s, *C*O_2Me); 138.9 (d, *J* 41, C_{ipso}); 133.7–128.8 (m, Ph); 132.1 (d, *J* 36, C_{ipso}); 93.0 (s, Cp); 51.8 (s, CO_2*Me*); 50.9 (s, CO_2*Me*); 40.4 (s, *C*OCCO_2Me); 40.4 (s, *C*HCO_2Me); 14.2 (d, *J* 15, PMe). ^{31}P NMR: 29.1 ppm. Mass spectrum *m/z* 560 (M^+). Anal. Calc. for $C_{26}H_{25}MoO_6P$: C, 55.73; H, 4.50. Found: C, 55.54, H, 4.49%.

Data for **4a**: IR: ν(CO) 1959m, 1877s, 1706m cm^{-1}. ^1H NMR: δ 7.60–7.33 (m, 10H, Ph); 6.13 (s, 1H, CHCO_2Me); 4.89 (d, J_{PH} 1.5, 5H, Cp); 3.81 (s, 3H, CO_2Me); 3.63 (s, 3H, CO_2Me); 2.15 (d, J_{PH} 7.6, 3H, PMe). ^{13}C NMR: δ 236.3 (d, *J* 26, CO); 178.5 (d, *J* 33, Mo*C*CO_2Me); 161.9 (s, *C*O_2Me); 161.9 (s, *C*O_2Me); 136.6 (d, *J* 45, C_{ipso}); 132.4 (s, *C*HCO_2Me); 131.6–128.7 (m, Ph); 93.7 (s, Cp); 50.9 (s, CO_2*Me*); 50.8 (s, CO_2*Me*); 20.9 (d, *J* 35, PMe). ^{31}P NMR: 48.7 ppm. Mass spectrum *m/z* 532 (M^+−CO). Anal. Calc. for $C_{26}H_{25}MoO_6P$: C, 55.73; H, 4.50. Found: C, 54.77; H, 4.56%.

*5.3. Synthesis of [CpMo(η³-COCH=CHCO₂Me)(CO)(PPh₂Me)] (**3b**) and [CpMo(CO)₂(CH=CHCO₂Me)(PPh₂Me)] (**4b**)*

In a similar manner, a solution of the anion $[CpMo(CO)_2(PPh_2Me)]^-$ generated by stirring $[Cp_2Mo_2(CO)_4(PPh_2Me)_2]$ (1.00 g, 1.12 mmol) in THF (40 cm^3) with an excess of sodium amalgam (0.3 g, 13.0 mmol Na in 5 cm^3 Hg), was treated sequentially with methyl propiolate (0.21 cm^3, 2.36 mmol) and $[Et_2NH_2][Br]$ (0.37 g, 2.40 mmol). Column chromatography as above gave the vinyl complex **4b** as a yellow band eluted in dichloromethane (40 mg, 3.5%) followed by a dark orange band of acryloyl complex **3b** (330 mg, 29%). Yields for this reaction were consistently lower than for the other three reported here.

Data for **3b**: IR: ν(CO) 1959m, 1733m cm^{-1}. ^1H NMR: δ 7.68–7.27 (m, 10H, Ph); 4.84 (d, J_{PH} 0.8, 5H, Cp); 3.62 (s, 3H, CO_2Me); 3.08 (dd, J_{PH} 11.3, J_{HH} 5.4, 1H, CHCO_2Me); 1.87 (d, J_{PH} 7.3, 3H, PMe); 1.79 (dd, J_{PH} 2.1, J_{HH} 5.4, 1H, COCH). ^{13}C NMR: δ 258.2 (d, *J* 15, acyl CO); 239.1 (d, *J* 15, CO); 178.0 (s, *C*O_2Me); 135.1 (d, *J* 38, C_{ipso}); 134.4–127.9 (m, Ph); 92.2 (s, Cp); 50.9 (s, CO_2*Me*); 44.5 (d, *J* 4, *C*HCO_2Me); 29.7 (s, CO*C*H); 17.7 (d, *J* 29, PMe). ^{31}P NMR: 37.4 ppm. Mass spectrum *m/z* 502 (M^+). Anal. Calc. for $C_{24}H_{23}MoO_4P$: C, 57.38; H, 4.61. Found: C, 56.25; H, 4.74%.

Data for **4b**: IR: ν(CO) 1953m, 1870s, 1693m cm^{-1}. ^1H NMR: δ 9.89 (dd, J_{PH} 1.8, J_{HH} 16.8, 1H, MoCH); 7.47–7.28 (m, 10H, Ph); 6.34 (dd, J_{PH} 0.8, J_{HH} 16.8, 1H, CHCO_2Me); 4.99 (d, J_{PH} 1.3, 5H, Cp); 3.66 (s, 3H, CO_2Me); 2.14 (d, J_{PH} 8.2, 3H, PMe). ^{13}C NMR: δ 232.9 (d, *J* 24, CO); 179.8 (d, *J* 11, Mo*C*H); 163.5 (s, *C*O_2Me); 137.1 (d, *J* 43, C_{ipso}); 132.0 (s, *C*HCO_2Me); 131.6–128.4 (m, Ph); 93.3 (s, Cp); 50.6 (s, CO_2*Me*); 21.0 (d, *J* 34, PMe). ^{31}P NMR: 48.5 ppm. Mass spectrum *m/z* 502 (M^+). Anal. Calc. for $C_{24}H_{23}MoO_4P.0.5CH_2Cl_2$: C, 54.01; H, 4.44. Found: C, 53.76; H, 4.34%.

*5.4. Synthesis of [CpMo{η³-COC(CO₂Me)=CHCO₂Me}(CO)(PPh₂Et)] (**3c**) and [CpMo(CO)₂{σ-C(CO₂Me)=CHCO₂Me}(PPh₂Et)] (**4c**)*

An olive-green solution of $Na[CpMo(CO)_2(PPh_2Et)]$ was prepared by reduction of $[Cp_2Mo_2(CO)_4(PPh_2Et)_2]$ (1.00 g, 1.16 mmol) in 40 cm^3 freshly distilled THF with an excess of sodium amalgam (0.30 g, 13.0 mmol of sodium in 5 cm^3 mercury). The solution was syringed into a second Schlenk tube and treated with DMAD (0.40 cm^3, 3.25 mmol), causing a colour change to red-brown. After stirring for 10 min, diethylammonium bromide (0.51 g, 2.97 mmol) was added. After 20 min, the solvent was removed. Column chromatography, eluting with acetone/dichloromethane (1:99) produced a yellow band consisting of the vinyl complex $[CpMo(CO)_2\{\sigma\text{-}C(CO_2Me)=CHCO_2Me\}(PPh_2Et)]$ (**4c**) (40 mg, 3.2%). Further elution with a 1:19 mixture of the same solvents gave an orange band containing the acryloyl compound $[CpMo\{\eta^3\text{-}COC(CO_2Me)=CHCO_2Me\}(CO)(PPh_2Et)]$ (**3c**) (620 mg, 49.6%).

Data for **3c**: IR: ν(CO) 1950s, 1729s, 1692m cm^{-1}. ^1H NMR: δ 7.60–7.32 (m, 10H, Ph); 4.72 (s, 5H, Cp); 3.64 (d, J_{PH} 11.5, 1H, CH); 3.60 (s, 3H, CO_2Me); 3.58 (s, 3H, CO_2Me); 2.20 (m, 1H, CH_2); 2.04 (dq, J_{PH} 2.7, J_{HH} 7.3, 1H, CH_2); 0.90 (dt, J_{PH} 15.0, J_{HH} 7.3, 3H, Me of Et). ^{13}C NMR: δ 252.2 (d, *J* 6, acyl CO); 236.0 (d, *J* 14, CO); 177.1 (s, *C*O_2Me); 172.9 (s, *C*O_2Me); 133.9 (d, *J* 40, C_{ipso});

133.6–128.5 (m, Ph); 132.0 (d, *J* 35, C_{ipso}); 93.1 (s, Cp); 51.7 (s, CO_2Me); 50.8 (s, CO_2Me); 40.6 (d, *J* 4, $CHCO_2Me$); 33.2 (s, $COCCO_2Me$); 21.7 (d, *J* 22, CH_2); 8.6 (d, *J* 5, Me of Et). ^{31}P NMR: 40.8 ppm. Mass spectrum *m*/*z* 575 $(M+H)^+$. Anal. Calc. for $C_{27}H_{27}MoO_6P$: C, 56.45; H, 4.70. Found: C, 55.94; H, 4.60%.

Data for **4c**: IR: ν(CO) 1960m, 1875s, 1705w cm^{-1}. ^{1}H NMR: δ 7.60–7.35 (m, 10H, Ph); 6.16 (s, 1H, CH); 4.81 (d, J_{PH} 1.2, 5H, Cp); 3.76 (s, 3H, CO_2Me); 3.59 (s, 3H, CO_2Me); 2.57 (dq, J_{PH} 7.8, J_{HH} 7.8, 2H, CH_2); 1.01 (dt, J_{PH} 18.0, J_{HH} 7.8, 3H, Me of Et). ^{13}C NMR: δ 236.8 (d, *J* 26, CO); 179.1 (d, *J* 53, Mo*C*CO_2Me); 161.8 (s, 2 *C*O_2Me); 135.0 (d, *J* 41, C_{ipso}); 132.0–128.3 (m, Ph); 93.9 (s, Cp); 50.9 (s, CO_2Me); 50.8 (s, CO_2Me); 26.4 (d, *J* 33, CH_2); 8.8 (d, *J* 2, Me of Et). ^{31}P NMR: 59.3 ppm. Mass spectrum *m*/*z* 574 (M^+). Anal. Calc. for $C_{27}H_{27}MoO_6P.0.25CH_2Cl_2$: C, 54.95; H, 4.65. Found: C, 54.79; H, 4.90%.

5.5. Synthesis of [CpMo(η^3-COCH=CHCO$_2$Me)(CO)(PPh$_2$Et)] (3d) and [CpMo(CO)$_2$(σ-CH=CHCO$_2$Me)(PPh$_2$Et)] (4d)

A solution of Na[CpMo(CO)$_2$(PPh$_2$Et)] was prepared by reduction of [$Cp_2Mo_2(CO)_4(PPh_2Et)_2$] (900.7 mg, 1.026 mmol) in 40 cm^3 freshly distilled THF with an excess of sodium amalgam (0.32 g, 13.9 mmol of sodium in 5 cm^3 mercury). The solution was syringed away from the amalgam into another Schlenk tube and methyl propiolate (0.18 cm^3, 2.025 mmol), was added, causing the solution to turn to a red/brown colour. After stirring 10 min 2.1 equiv. of diethylammonium bromide (330.2 mg, 2.143 mmol) was added to the solution and it was stirred for 20 min. No noticeable colour change was observed. The solvent was removed on a rotary evaporator and the products of the reaction were separated by column chromatography. A yellow band was eluted in pure dichloromethane and shown to be the vinyl compound, [CpMo(σ-CH=CHCO$_2$Me)(CO)$_2$(PPh$_2$Et)] (**4d**), followed by a brown band in acetone/dichloromethane (3:17), shown to be the acryloyl product, [CpMo(η^3-COCH=CHCO$_2$Me)(CO)(PPh$_2$Et)] (**3d**). Final yields of the two isomeric products were 24.1 mg (2.6%) and 308.8 mg (33.2%), respectively.

Data for **3d**: IR: ν(CO) 1957s, 1721m, 1677m cm^{-1}. ^{1}H NMR: δ 7.78–7.07 (m, 10H, Ph); 4.88 (s, 5H, Cp); 3.61 (s, 3H, Me); 3.02 (dd, J_{PH} 10.8, J_{HH} 5.3, 1H, COCH); 2.45 (m, 1H, CH_2); 2.25 (m, 1H, CH_2); 1.54 (dd, J_{PH} 2.0, J_{HH} 5.3, 1H, $CHCO_2Me$); 0.96 (dt, J_{PH} 17.4, J_{HH} 7.8, 3H, Me of Et). ^{13}C NMR: δ 258.3 (d, *J* 5, acyl CO); 239.5 (d, *J* 15, CO); 177.7 (s, *C*O_2Me); 133.8–128.2 (m, Ph); 91.8 (s, Cp); 50.8 (s, *C*O_2Me); 44.4 (d, *J* 3, *C*HCO_2Me); 25.1 (d, *J* 28, CH_2); 23.6 (s, CO*C*H); 8.5 (s, Me of Et). ^{31}P NMR: 49.3 ppm. Mass spectrum *m*/*z* 516 (M^+). Anal. Calc. for $C_{25}H_{25}MoO_4P$: C, 58.14; H, 4.84. Found: C, 58.12; H, 4.90%.

Data for **4d**: IR: ν(CO) 1953w, 1870m, 1682m cm^{-1}. ^{1}H NMR: δ 9.90 (dd, J_{PH} 1.1, J_{HH} 16.5, 1H, MoCH); 7.78–7.42 (m, 10H, Ph); 6.37 (d, J_{HH} 16.5, 1H, CH); 4.94 (d, J_{PH} 1.2, 5H, Cp); 3.68 (s, 3H, CO_2Me); 2.62 (dq, J_{PH} 7.8, J_{HH} 7.8, 2H, CH_2); 1.09 (dt, J_{PH} 18.0, J_{HH} 8.0, 3H, Me of Et). ^{13}C NMR: δ 233.5 (d, *J* 24, CO); 180.9 (d, *J* 11, Mo*C*H); 163.5 (s, *C*O_2Me); 135.5 (d, *J* 41, C_{ipso}); 132.3–128.3 (m, Ph); 93.4 (s, Cp); 50.6 (s, CO_2Me); 26.4 (d, *J* 32, CH_2); 8.8 (s, Me of Et). ^{31}P NMR: 59.4 ppm. Mass spectrum *m*/*z* 516 (M^+). Anal. Calc. for $C_{25}H_{25}MoO_4P$: C, 58.14; H, 4.84. Found: C, 57.78; H, 4.71%.

Table 3
Summary of crystallographic data for complexes **3b** and **4b**

	3b	**4b**
Empirical formula	$C_{24}H_{23}MoO_4P$	$C_{24}H_{23}MoO_4P$
Formula weight	502.33	502.33
T (K)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	7.598(2)	9.2168(7)
b (Å)	14.725(4)	10.4978(8)
c (Å)	19.458(6)	11.8163(10)
α (°)	90	75.969(3)
β (°)	97.869(5)	89.314(3)
γ (°)	90	81.540(4)
V (Å^3)	2156.4(10)	1096.79(15)
Z	4	2
D_{calc} (Mg m^{-3})	1.547	1.521
μ (mm^{-1})	0.710	0.698
F(000)	1024	512
Crystal size (mm^3)	0.35 × 0.21 × 0.12	0.28 × 0.12 × 0.09
θ Range for data collection (°)	1.74–25.00	1.78–25.00
Reflections collected	20239	17062
Independent reflections	3789 [*R*(int) = 0.1701]	3861 [*R*(int) = 0.0200]
Data/restraints/parameters	3789/159/273	3861/151/275
Goodness-of-fit on F^2	0.960	1.353
Final R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0630$, $wR_2 = 0.1300$	$R_1 = 0.0523$, $wR_2 = 0.1612$
All data	$R_1 = 0.1061$, $wR_2 = 0.1445$	$R_1 = 0.0524$, $wR_2 = 0.1613$
Largest diffraction peak and hole (e Å^{-3})	0.878 and −1.027	0.663 and −1.649

6. Crystal structure determinations

The crystal data for the two structures are collected in Table 3. General procedures were as described in previous publications. A Bruker Smart CCD area detector with Oxford Cryosystems low temperature system was used for data collection at 150(2) K. Complex scattering factors were taken from the program package SHELXTL [19] as implemented on a Viglen Pentium computer. Hydrogen atoms were placed geometrically and refined in riding mode (including torsional freedom for methyl groups) with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom (1.5 for methyl groups).

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Appendix A. Supplementary material

CCDC 665423 and 665422 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.059.

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