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# Lithiation of diynyl—ruthenium complexes: Routes to novel metallated functional diynes

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#### ABSTRACT

Conditions for the efficient lithiation of the diynyl group in complexes  $Ru(C \equiv CC \equiv CH)(PP)Cp'$  [(PP)  $Cp' = (dppe)Cp^*$  **1**,  $(PPh_3)_2Cp$  **2**] have been investigated. Addition of two equiv. LiBu to the diynyl complexes in thf solution at  $-78^{\circ}C$  effects rapid conversion to putative  $Ru(C \equiv CC \equiv CLi)(PP)Cp'$ . Assays using subsequent reactions with either SiClMe<sub>3</sub> or AuCl(PPh<sub>3</sub>) indicate that up to 80% conversion can be achieved. Reactions of the lithiated species with organic electrophiles [MeI, MeC(O)Cl, PhC(O)Cl, ClC(O) OMe, PhCHO, Ph<sub>2</sub>CO] and metal-containing substrates [MCIPh<sub>3</sub> (M = Ge, Sn), *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuCl(PPh<sub>3</sub>), (AuCl)<sub>2</sub>( $\mu$ -dppm)] proceed to give functionalised diynyl complexes or bimetallic derivatives which are accessible only with difficulty or not at all from the parent diynes. Single-crystal X-ray diffraction molecular structures of  $Ru(C \equiv CC \equiv CR)(dppe)Cp^*$  (R = Me, GePh<sub>3</sub>) are reported: there is significantly greater delocalisation along the  $Ru-C_4-R$  chain in the GePh<sub>3</sub> derivative.

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# 1. Introduction

Although lithiated alkynes and poly-ynes have proved to be useful reagents for the syntheses of other compounds through their reactions with electrophiles [1], there have been relatively few accounts of the lithiation of metalla-alkynes, poly-ynes and other carbon-rich complexes. These intermediates would provide access to a wide variety of functionalised complexes which are accessible with difficulty or not at all from the parent alkynes or poly-ynes. Examples of all-carbon ligands which have been successfully metallated and subsequently derivatised include C, C<sub>2</sub> and C<sub>4</sub> species include:

(a) *Carbenes.* Fischer-type ethynyl-carbene complexes HC≡CC(NMe<sub>2</sub>)=M(CO)<sub>5</sub> (M = Cr, W) have been metallated with LiBu, subsequent reactions with a range of Main Group halides (BBr<sub>3</sub>, SiCl<sub>4</sub>, GeCl<sub>4</sub>, SnCl<sub>4</sub>, PCl<sub>3</sub>) affording E{C≡CC (NMe<sub>2</sub>)=W(CO)<sub>5</sub>}<sub>X</sub> (E = B, P, x = 3, E = Si, Ge, S, x = 4). and L<sub>n</sub>M {C≡CC(NMe<sub>2</sub>)=M(CO)<sub>5</sub>} [L<sub>n</sub>M = *trans*-FeCl(dmpe)<sub>2</sub>, *trans*-PdCl(PEt<sub>3</sub>)<sub>2</sub>, *trans*-PdCl(C≡CH)(PEt<sub>3</sub>)<sub>2</sub>, Au(PPh<sub>3</sub>), to give mono-substituted products; TiCl<sub>2</sub>Cp<sub>2</sub>, *trans*-FeCl<sub>2</sub>(dmpe)<sub>2</sub>, MCl<sub>2</sub> (PEt<sub>3</sub>)<sub>2</sub> (M = Ni, Pd, Pt), HgCl<sub>2</sub>, to give disubstituted complexes] [2,3]. Isomerisation of the Au(PPh<sub>3</sub>) derivative to (Ph<sub>3</sub>P)

AuC(NMe<sub>2</sub>)=C=C=M(CO)<sub>5</sub> occurs upon standing in solution [3]. Extension of the carbon chain was achieved by reaction of the ethynylcarbene with LiBu/I<sub>2</sub> to give IC=CC(NMe<sub>2</sub>)= M(CO)<sub>5</sub>, followed by Cu(I)-catalysed coupling with IC=C-C=CSiMe to give  $(OC)_5W=C(NMe_2)(C=C)_3SiMe_3$ , desilylation and reaction with LiBu/HgCl<sub>2</sub> to give Hg { $(C=C)_3C(NMe_2)=W(CO)_5$ }.

(b) Vinylidenes. Deprotonation of [Ru(=C=CH<sub>2</sub>)P<sub>2</sub>Cp<sup>\*</sup>]<sup>+</sup> (P = PMe<sub>3</sub>, PPh<sub>3</sub>) with KOBu<sup>t</sup> gives Ru(C≡CH)P<sub>2</sub>Cp<sup>\*</sup> which with LiBu or LiBu<sup>t</sup> is further deprotonated to LiC≡CRuP<sub>2</sub>Cp<sup>\*</sup>. The lithio derivative reacts with ECl (E = SiMe<sub>3</sub>, GeMe<sub>3</sub>, SnBu<sub>3</sub>, PPh<sub>2</sub>) to give Ru(C≡CE)P<sub>2</sub>Cp<sup>\*</sup> [4]. Double or triple deprotonation of [Ru(=C=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cp]<sup>+</sup> occurs with more than one equiv. LiBu<sup>t</sup>, as shown by subsequent reactions with Mel or SiClMe<sub>3</sub> [5]. Metallation of Ru(C≡CH)(PPh<sub>3</sub>)<sub>2</sub>Cp with LiBu, or treatment of [Ru(=C=CH<sub>2</sub>)(dppe)Cp<sup>\*</sup>]<sup>+</sup> with two equivalents of LiBu, followed by addition of PhOCN, gave Ru(C≡CCN)(PPh<sub>3</sub>)<sub>2</sub>Cp and Ru(C≡CCN)(dppe)Cp<sup>\*</sup>, respectively [6].

Related reactions were reported earlier, when addition of LiMe to  $Mn(\eta-HC_2CO_2Me)(CO)_2Cp$  followed by quenching with electrophiles (MeOTf) afforded  $Mn(=C=CMe_2)(CO)_2Cp$  in a reaction thought to proceed via loss of Me<sub>2</sub>CO from an intermediate Li<sub>2</sub>[Mn  $\{=C=CC(O)Me_2\}(CO)_2Cp\}$  to give Li<sub>2</sub>[Mn(=C=C)(CO)\_2Cp] [7].

(c) *Carbynes*. Lithiocarbynes  $LiC \equiv M(CO)_2 Tp^*$  [M = Mo, W;  $Tp^* = HB(Me_2-pz)_3$ ] have been obtained directly from

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 $M(\equiv CBr)(CO)_2Tp^*$  and LiBu [8], or from  $HC\equiv W(CO)_2Tp^*$  with LiBu, LiBu<sup>t</sup> or solid LiNMe<sub>2</sub> (LDA) [9]. Further reactions with electrophiles I<sub>2</sub>, Mel, SiMe<sub>3</sub>(OTf), Ph<sub>2</sub>C=O, PhCHO and PhCOBr [9] or with NBS, H<sub>2</sub>O, Mel, SiMe<sub>3</sub>Cl, Ph<sub>2</sub>S<sub>2</sub>, Ph<sub>2</sub>Se<sub>2</sub>, Se<sub>n</sub>, Te<sub>n</sub> and FeCl(CO)<sub>2</sub>Cp [8] were reported. More recently, detailed insights into reactions of the supposed metallated carbynes suggest that not only competitive reactions between side-products, such as BuBr (which can act as proton donor or nucleophile), but oxidation [single-electron transfer to give a radical carbide complex Mo( $\equiv$ C•)(CO)<sub>2</sub>Tp<sup>\*</sup>] may occur [10].

(d) *Alkynyls.* The synthesis of {W(CO)<sub>3</sub>Cp}<sub>2</sub>C<sub>2</sub> from LiC=CH and WX(CO)<sub>3</sub>Cp (X = Cl, Br) proceeds via the putative intermediate LiC=CW(CO)<sub>2</sub>Cp [11]. Lithiation of Re(C=CH)(NO)(PPh<sub>3</sub>)Cp with LiBu gives LiC=CRe(NO)(PPh<sub>3</sub>)Cp, which reacts with electrophiles (D<sub>2</sub>O, MeI, ClSiMe<sub>3</sub>, ClSnPh<sub>3</sub>) or with *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> and *trans*-PdCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> to give mixed-metal derivatives [12]. With more than one equivalent of LiBu, both the ethynyl group and the Cp ring are metallated, as shown by reactions with MeI or SnClPh<sub>3</sub>. The analogous Cp<sup>\*</sup> complex gave only LiC=CRe(NO)(PPh<sub>3</sub>)Cp<sup>\*</sup> [13]. Reactions of LiC=C-Re(NO)(PPh<sub>3</sub>)Cp with W(CO)<sub>6</sub>, Mn(CO)<sub>3</sub>Cp' (Cp' = Cp,  $\eta$ -C<sub>5</sub>HCl<sub>4</sub>,  $\eta$ -C<sub>5</sub>Cl<sub>5</sub>) and Fe(CO)<sub>5</sub>, followed by addition of [Me<sub>3</sub>O] BF<sub>4</sub>, gave the corresponding carbene complexes [14].

Lithiation of Fe(C=CH)(dppe)Cp\* with LiMe or LiBu<sup>t</sup> and treatment with PClPh<sub>2</sub> gave Fe(C=CPPh<sub>2</sub>)(dppe)Cp\*, the dppe ligand also being metallated with an excess of LiR [15]. Metallation of M(C=CH)(PP)(L') [M = Fe, (PP) = dppm, L' = Cp; M = Ru, L' =  $\eta^5$ -C<sub>9</sub>H<sub>7</sub>, (PP) = (PMe<sub>3</sub>)(PPh<sub>3</sub>), (PPh<sub>3</sub>)<sub>2</sub>, dppe] occurs with LiBu<sup>t</sup> at -78 °C. All react with MeOTf to give vinylidenes [M(=C=CMe<sub>2</sub>)(PP)L']OTf and with SnClPh<sub>3</sub> to give M(C=CSnPh<sub>3</sub>)(PP)(L'). With [I(py)<sub>2</sub>]BF<sub>4</sub>, Ru(C=CI)(PP)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>) [(PP) = (PPh<sub>3</sub>)<sub>2</sub>, dppe] were formed [16].

(e) Diynyls and triynyls. Deprotonation of W(C≡CC≡CH)(CO)<sub>3</sub>Cp is achieved with bulky LDA, smaller LiR reagents attacking the CO groups. Orange LiC≡CC≡CW(CO)<sub>3</sub>Cp reacts with SiClMe<sub>3</sub> and MnCl(CO)<sub>5</sub> to give the silylated and manganated diynyl complexes, respectively [17]. The reaction between Li<sub>2</sub>C<sub>4</sub>(thf)<sub>n</sub> and *fac*-W(CO)<sub>3</sub>(dppe)(thf) afforded [Li(thf)<sub>2</sub>]<sub>2</sub>[{(dppe)(OC)<sub>3</sub>W}<sub>2</sub> (C≡CC≡C)] which was successfully employed as a precursor for novel derivatives containing the W≡CC≡CC≡W moiety [18].

Crude Re(C=CC=CLi)(NO)(PPh<sub>3</sub>)Cp can be isolated as an orange solid after reaction of LiBu with Re(C=CC=CH)(NO)(PPh<sub>3</sub>) Cp in thf/hexane; subsequent reactions with *trans*-RhCl(CO) (PPh<sub>3</sub>)<sub>2</sub> and *trans*-PdCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> gave the expected mixed Re-Rh and Re-Pd complexes, the latter being accompanied by *trans*-Pd {C=CC=C[Re(NO)(PPh<sub>3</sub>)Cp]}<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> [12b]. Reactions of the lith-iodiyne with Fe(CO)<sub>5</sub>, Mn(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>X<sub>5</sub>) (X = Cl, Br) or Mn(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>4</sub>Cl), followed by [OMe<sub>3</sub>]BF<sub>4</sub>, gave the corresponding carbene complexes, the latter being accompanied by Re(C=CC=CMe) (NO)(PPh<sub>3</sub>)Cp [14]. Treatment of Re{(C=C)<sub>x</sub>H}(NO)(PPh<sub>3</sub>)Cp\* (*n* = 2, 3) with Cul in the presence of LiBu afforded Re{(C=C)<sub>x</sub>Cu} (NO)(PPh<sub>3</sub>)Cp\* [19].

Metallation of  $Fp^*C \equiv CC \equiv CH$  [ $Fp^* = Fe(CO)_2Cp^*$ ] with LiBu<sup>s</sup>, followed by reaction with  $Fp^*Cl$ , gave  $Fp^*_2C_4$  [20]. Lithio derivatives of  $Fe(C \equiv CC \equiv CH)(CO)(L)Cp$  (L = CO, PPh<sub>3</sub>) react with SiClMe<sub>3</sub> and MX(CO)<sub>3</sub>Cp (M = Mo, W) [21].

Generally it was found that as the carbon chain lengthens, the lithio derivatives are progressively less nucleophilic and/or basic. Relative  $pK_a$  values of  $W(\equiv CH)(CO)_2Tp^*$  [7] and  $Re(C\equiv CH)(NO)$  (PPh<sub>3</sub>)Cp' (Cp' = Cp, Cp\*) are 28.7 and 22–34 (all in thf), those of the Re compounds being higher than analogous organo-lithio carbons [13].

(f) Alkynes. Treatment of Co<sub>2</sub>(µ-HC≡CSiMe<sub>3</sub>)(CO)<sub>6</sub> with LiNR<sub>2</sub> is reported to give dark green-black Co<sub>2</sub>(µ-LiC≡CSiMe<sub>3</sub>)(CO)<sub>6</sub>, as indicated by formation of {Co<sub>2</sub>(CO)<sub>6</sub>}<sub>n</sub>(Me<sub>3-</sub> SiC≡CC≡CSiMe<sub>3</sub>) (*n* = 1, 2) with electrophiles as a result of reactions involving single electron transfer. Similarly, {Co<sub>2</sub>(CO)<sub>6</sub>}<sub>2</sub>(LiC≡CC≡C−SiMe<sub>3</sub>) afforded the diyne dimer {Co<sub>2</sub>(CO)<sub>6</sub>}<sub>3</sub>{Me<sub>3</sub>Si(C≡C)<sub>4</sub>SiMe<sub>3</sub>} [22].

The molecular structures of the lithiated species are generally unknown with the exception of Berke's W complex (above), for which the crystal structure revealed that two  $\text{Li}(\text{thf})_2$ moieties are also each coordinated in  $\pi$ -fashion by C=C and C=O groups [18].

Continuing our studies of diynyl complexes containing Ru(PP) Cp' [(PP)Cp' = (PPh\_3)\_2Cp, (dppe)Cp, (dppe)Cp\*], we have begun a study of the deprotonation of the C=CC=CH group with a view to forming functionalised derivatives (containing either organic or metallic groups) which cannot easily be obtained from the parent diynes. The following describes initial studies into the lithiation of the diynyl ligands, together with some studies of their further reactions with organic and metal-containing electrophiles. We have reported reactions between LiC=CC=CRu(dppe)Cp\* and 1,2-C\_5F\_6Cl\_2 to give 1-ClC\_5F\_6-2-C=CC=CRu(dppe)Cp\* and with the polyfluoroaromatics C\_6F\_5X (X = F, OMe, CN, NO\_2) and C\_{10}F\_8 during the course of this work [23].

# 2. Results and discussion

2.1. Lithiation of Ru(C≡CC≡CH)(PP)Cp' [(PP)Cp' = (dppe)Cp\* **1**, (PPh<sub>3</sub>)<sub>2</sub>Cp **2**]

Previous work has shown that lithiation of terminal metallaalkynes and metalla-diynes proceeds with strong bases (LiBu, LiMe, LiBu<sup>t</sup>), although the presence of other electrophiles, such as CO, can result in preferential attack on these centres [17]. With the complexes Ru(C $\equiv$ CC $\equiv$ CH)(PP)Cp' [(PP)Cp' = (PPh\_3)<sub>2</sub>Cp, (dppe)Cp, (dppe)Cp\*] the alternative sites of proton abstraction are the Cp' groups or the dppe ligand. In some cases, it has been shown that this problem can be overcome by the use of sterically bulky organolithiums, such as LDA.

In the present work, we report the lithiation of the diynyl ligands in Ru(C $\equiv$ CC $\equiv$ CH)(PP)Cp' [(PP)Cp' = (dppe)Cp\* **1**, (PPh<sub>3</sub>)<sub>2</sub>Cp **2**] using LiBu, LiMe or LDA at  $-78 \degree$ C (Eq. (1)).

$$Ru(C \equiv CC \equiv CH)(PP)Cp' + LiR \rightarrow LiC \equiv CC \equiv CRu(PP)Cp'$$
(1)

The initial bright yellow solution of the metalladiyne rapidly darkens after addition of the organo-lithium reagent, and we assume that the anion  $Ru(C \equiv CC \equiv C^{-})(PP)Cp$  (or the ion-pair  $[Li(solv)^+][Ru(C \equiv CC \equiv C^-)(PP)Cp']; solv = thf, OEt_2)$  is present in these solutions. The <sup>31</sup>P NMR spectrum of  $Ru(C \equiv CC \equiv CH)(dppe)$ Cp\* in thf- $d_8$  at -78 °C contains a single resonance at  $\delta$  80.7. After addition of two equiv. of LiBu, there is now a single peak at  $\delta$  82.9. The <sup>1</sup>H NMR spectrum of the diyne contains a singlet for the CH proton at  $\delta$  1.34, other resonances for the Cp<sup>\*</sup> ( $\delta$  1.59), dppe ( $\delta$ 2.15–2.17, 2.71–2.76) and Ph groups ( $\delta$  7.25–7.78) also being present. After lithiation, minor shifts of ca 0.05 ppm in the latter peaks are accompanied by a larger shift of the CH resonance to  $\delta$  1.68 and a decrease in its relative intensity, suggesting that only partial lithiation had occurred. Addition of an excess of organolithium reagent resulted in considerable broadening of this region, precluding further analysis. These small differences in chemical shifts are not conclusive evidence for metallation and give no information about the structure of the putative  $Ru(C \equiv CC \equiv C - Li)(dppe)Cp^*$  derivative 3.

Although we have not been able to characterise these species directly, addition of electrophiles, such as SiClMe<sub>3</sub>, to the lithiated diynyls affords the expected stable silyldiynes  $Ru(C \equiv CC = C-SiMe_3)(PP)Cp'$  [(PP)Cp' = (dppe)Cp\* **4**, (PPh<sub>3</sub>)<sub>2</sub>Cp **5**] in 60–80% isolated yields. This reaction serves as a means of assaying the progress of the lithiation under various conditions. Further exploration of the lithiation of  $Ru(C \equiv CC \equiv CH)(PP)Cp'$  was achieved by using one or two equiv. LiR (R = Me, Bu, NMe<sub>2</sub>) and assaying progress of the reaction by isolation of the  $Ru(C \equiv CC \equiv CSiMe_3)(PP)Cp'$  formed after addition of SiClMe<sub>3</sub>. Some results of reactions carried out under a variety of conditions are given in Table 1. Yields of between 59 and 86% were reproducibly obtained. The earlier syntheses of the silyldiynes were achieved by reaction of RuCl(PP)Cp' with  $HC \equiv CC \equiv CSiMe_3$  in thf in the presence of Na[BPh<sub>4</sub>] and NEt<sub>3</sub> at 50 °C [24].

A limited range of similar experiments was also carried out using AuCl(PPh<sub>3</sub>) as the electrophile, isolated yields of Ru {C=CC=CAu(PPh<sub>3</sub>)}(PP)Cp' [(PP)Cp' = (dppe)Cp\* **6**, (PPh<sub>3</sub>)<sub>2</sub>Cp **7**] ranging between 56 and 85% (Table 2). The gold complexes have been obtained previously in 93 and 69% yields, respectively, from reactions between Ru(C=CC=CH)(PP)Cp' and AuCl(PPh<sub>3</sub>) in the presence of K[N(SiMe<sub>3</sub>)<sub>2</sub>] in th fat r.t. [24]. We have found that the "best" conditions for the lithiation of the diynyls involve the addition of two equivalents of organolithium reagent at -78 °C in thf as solvent, followed by warming to room temperature, cooling again to -78 °C and addition of the electrophile. Reactions are completed by a final warming to room temparature prior to workup and isolation of the product.

As implied above, we have not been able to isolate the lithiated diynyl-ruthenium complexes and so have not been able to determine their molecular structures by single-crystal XRD studies, for example. However, two recent examples of lithiated alkynyl compounds provide some pointers to possible molecular arrangements. Kira et al. [25] have reported the molecular structure of the

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Selected bond parameters for  $Ru(C \equiv CC \equiv CR)(dppe)Cp^*$  (R = Me, GePh<sub>3</sub>).

Complex	8	13
Bond distances (Å)		
Ru-P(1)	2.2616(6)	2.2778(7)
Ru–P(2)	2.2731(5)	2.2726(7)
Ru–C(cp)	2.236-2.273(2)	2.238-2.286(2)
(av.)	2.26	2.259
Ru-C(1)	2.038(2)	1.975(3)
C(1)-C(2)	1.150(3)	1.224(3)
C(2)–C(3)	1.428(3)	1.377(3)
C(3)–C(4)	1.192(3)	1.209(3)
C(4)-X	1.474(3)	1.881(3)
Bond angles (°)		
P(1)-Ru-P(2)	82.57(2)	82.73(2)
P(1)-Ru-C(1)	82.53(6)	79.23(7)
P(2)-Ru-C(1)	86.12(5)	89.02(7)
Ru-C(1)-C(2)	178.11(18)	176.5(2)
C(1)-C(2)-C(3)	173.7(2)	176.2(3)
C(2) - C(3) - C(4)	177.8(2)	179.0(3)
C(3)-C(4)-X	176.5(3)	165.5(2)

alkynylsilyl-lithium derivative LiSi(C $\equiv$ CSiMe<sub>3</sub>)(SiMe<sub>2</sub>Bu<sup>t</sup>) (**A**), which is a dimer containing one thf molecule attached to one Li atom, which is also attached to two Si(C $\equiv$ CSiMe<sub>3</sub>) groups by Li–Si bonds. The second Li atom is also attached to these Si atoms, as well as being  $\pi$ -bonded to the two C $\equiv$ C triple bonds.

A more relevant interaction is found for the two Li atoms in  $[\text{Li}(\text{thf})_2]_2[(\text{dppe})(\text{OC})_3\text{W}(C \equiv \text{CC} \equiv \text{C})\text{W}(\text{CO})_3(\text{dppe})]$  (**B**), which was obtained from  $\text{Li}_2\text{C}_4(\text{thf})_n$  and *fac*-W(CO)\_3(dppe)(thf) [18]. Here, each Li is tetrahedrally coordinated by two thf ligands and two  $\pi$ -type interactions with a C = C triple bond and a CO ligand.

Following these precedents, it is likely that the Li in  $LiC \equiv CC \equiv CRu(PP)Cp'$  is coordinated to a  $C \equiv C$  triple bond, with further interactions with a solvent molecule (thf) and either the phosphine or Cp' ligands



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LiR	Reagent	Solvent	Temperature/°C	Time <sup>a</sup>	Yield/% <sup>b</sup>
(a) Ru(C≡CC≡CH)(PPh <sub>3</sub> ) <sub>2</sub> Cp					
LiBu (1 eq)	SiClMe <sub>3</sub>	thf/hexane (1/1)	-40	1 h	74
LiBu (1 eq)	AuCl(PPh <sub>3</sub> )	thf/hexane (1/1)	-80	1 h	62
LiBu (2 eq)	SiClMe <sub>3</sub>	thf	-78	30 min	80
LiBu (2 eq)	AuCl(PPh <sub>3</sub> )	thf	-78	30 min	70
LiMe (1 eq)	SiClMe <sub>3</sub>	thf/hexane (2/1)	-20	1 h	74
LiMe (1 eq)	AuCl(PPh <sub>3</sub> )	thf/Et <sub>2</sub> O (1/1)	-20	1 h	56
LDA (1 eq)	SiClMe <sub>3</sub>	thf	-78	2 h	59
(b) Ru(C≡CC≡CH)(dppe)Cp*					
LiBu (1 eq)	SiClMe <sub>3</sub>	thf	-78	1 h	78
LiBu (1 eq)	AuCl(PPh <sub>3</sub> )	thf	-78	30 min	60
LiBu (2 eq)	SiClMe <sub>3</sub>	thf	-78	30 min	86
LiBu (2 eq)	AuCl(PPh <sub>3</sub> )	thf	-78	30 min	85
LiBu/tmeda (1 eq)	SiClMe <sub>3</sub>	thf/hexane (2/1)	-80	2 h	64
LiMe (2 eq)	SiClMe <sub>3</sub>	thf/hexane (1/1)	0	30 min	70
LiMe (2 eq)	AuCl(PPh <sub>3</sub> )	thf/hexane (2/1)	-20	30 min	64
LiBu <sup>t</sup> (1 eq)	SiClMe <sub>3</sub>	thf/Et <sub>2</sub> O (1/1)	-80	1 h	75
LDA	AuCl(PPh <sub>3</sub> )	thf/hexane (1/1)	-78	1 h	62

<sup>a</sup> After this time at the indicated temperature, the mixture was allowed to warm to r.t.

<sup>b</sup> Isolated yield of product.



Scheme 1. Some reactions of Li-C=CC=C-Ru(dppe)Cp\* with organic electrophiles.

The reactivity of the lithiated metalla-diynes was initially examined in a series of reactions with organic electrophiles on the one hand (Scheme 1), and with various metal halides on the other (Scheme 2). We have used the Ru(dppe)Cp\* as an electron-rich end-group for the various diynes, so that the work described below is largely limited to this system. However, related studies have shown that the  $Ru(PPh_3)_2Cp$  end-group affords similar complexes with *trans*-RhCl(CO)(PPh\_3)\_2 and {CuCl(PPh\_3)}\_4, also described below (Scheme 3).



Scheme 2. Some reactions of Li-C=CC=C-Ru(dppe)Cp\* with metal halides.



Scheme 3. Reactions of Ru(C=CC=CLi)(PPh<sub>3</sub>)<sub>2</sub>Cp with *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> and {CuCl(PPh<sub>3</sub>)<sub>2</sub>}.

#### 2.2. Reactions of Li-C $\equiv$ CC $\equiv$ C-Ru(dppe)Cp\* 3

Spectroscopic properties of the Ru(dppe)Cp\* fragment resemble those reported on numerous other occasions. In particular, the <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra contain resonances assigned to Cp\* [ $\delta_{\rm H}$  ca 1.50,  $\delta_{\rm C}$  ca 10.00 (Me), ca 93.00 (ring C), and  $\delta_{\rm P}$  ca 81.00 (dppe)]. Resonances between  $\delta_{\rm C}$  52 and 125 arise from C atoms in the C<sub>4</sub> chain, that with highest chemical shift being assigned to the Ru–C(1)= atom, and other signals with progressively lower chemical shift to C(2), C(3) and C(4) (numbering from the Ru atom), i.e., with increasing distance from the metal centre. Limited solubilities precluded our observing <sup>13</sup>C resonances for the C<sub>4</sub> chains in some cases. Other data arising from the functional groups are given in the separate discussions below.

# 2.3. Reactions with organic substrates

- (a) *Mel.* The reaction of Mel with a solution of Ru(C=CC=CLi)(dppe) Cp\* in thf at -78 °C afforded Ru(C=CC=CMe)(dppe)Cp\* **8** in 70% yield after conventional work-up. In addition to characteristic peaks for the Ru(dppe)Cp\* fragment, the Me group gave singlet resonances at  $\delta_H$  1.73 and  $\delta_C$  21.03, while the <sup>13</sup>C NMR spectrum also contained resonances at  $\delta_C$  52.46, 76.86, 91.73 and 124.69, assigned to the carbons of the C<sub>4</sub> chain. Two  $\nu$ (C=C) bands at 1908, 2029 cm<sup>-1</sup> are in the IR spectrum, while the electrospray mass spectrum (ES-MS) contains [M + MeOH]<sup>+</sup> at *m*/*z* 730. The molecular structure of **8** has been determined by a single-crystal X-ray diffraction study (below).
- (b) *MeC(O)Cl.* Bright yellow Ru{C≡CC≡CC(O)Me}(dppe)Cp\* 9 was obtained from the reaction between acetyl chloride and Ru(C≡CC≡CLi)(dppe)Cp\* in 60% yield. The Me group gives resonances at δ<sub>H</sub> 2.14, δ<sub>C</sub> 33.35, with the carbonyl group giving a singlet at δ<sub>C</sub> 201.57. The IR spectrum contains *v*(C≡C) at 2004, 2048 and *v*(CO) at 1710 cm<sup>-1</sup>, with M<sup>+</sup> at *m*/*z* 726 in the ES-MS.
  (c) *PhC(O)Cl.* An immediate colour change from yellow
- (c) PhC(O)Cl. An immediate colour change from yellow to red occurs when benzoyl chloride is added to Ru(C≡CC≡C-Li)(dppe)Cp\* in thf at −78 °C. The usual work-up afforded Ru{C≡CC≡CC(O)Ph}(dppe)Cp\* 10 as a red powder in

75% yield. Characteristic spectroscopic data include  $v(C \equiv C)$  at 2000, 2109 cm<sup>-1</sup> and v(CO) at 1716 cm<sup>-1</sup>, the latter group giving a singlet <sup>13</sup>C resonance at  $\delta_C$  206.41. The ES-MS contains M<sup>+</sup> and [M + Na]<sup>+</sup> at m/z 788 and 811, respectively.

- (d) *ClC*(*O*)*OMe*. The reaction of Ru(C=CC=CLi)(dppe)Cp\* with methyl chloroformate afforded Ru{C=CC=CC(O)OMe}(dppe)Cp\* **11** in 40% yield, the OMe group giving a singlet resonance at  $\delta_{\rm H}$  1.68, at somewhat higher field than normal, and  $\nu$ (CO) at 1723 cm<sup>-1</sup> in the IR spectrum; this complex is somewhat unstable in solution and neither a satisfactory microanalysis nor a <sup>13</sup>C NMR spectrum could be obtained. The ES-MS spectrum contains M<sup>+</sup> at *m*/*z* 742.
- (e) *PhCHO*. The reaction of benzaldehyde with **3** gave bright orange Ru{C=CC=CCHPh(OH)}(dppe)Cp\* **12**, distinguished by singlet CH and OH resonances at  $\delta_{\rm H}$  1.66 and 5.52, respectively. The CHPh(OH) group gives rise to a singlet at  $\delta_{\rm C}$  79.89. In the ES-MS, M<sup>+</sup> and [M + Na]<sup>+</sup> are found at *m*/*z* 790 and 813, respectively.

## 2.4. Reactions with metal halides

- (a) *GeCl(PPh<sub>3</sub>) and SnCl(PPh<sub>3</sub>)*. Following the ready synthesis of Ru(C=CC=CSiMe<sub>3</sub>)(dppe)Cp\* 4 during the assay experiments described above, reactions of the lithio-diyne with other Group 14 halides were attempted. Reactions with GeClPh<sub>3</sub> and SnClPh<sub>3</sub> afforded Ru(C=CC=CEPh<sub>3</sub>)(dppe)Cp\* (E = Ge 13, Sn 14) in 82 and 70% yields, respectively. Characterisation followed from their spectra (see Section 4) and the presence of ions at *m*/*z* 1009 ([M + Na]<sup>+</sup>) and 988 ([M + H]<sup>+</sup>) (for 13), and 1033 (M<sup>+</sup>) (for 14). The molecular structure of 13 was confirmed by a single-crystal X-ray diffraction study (below).
- (b) *cis-PtCl*<sub>2</sub>(*PPh*<sub>3</sub>)<sub>2</sub>. A similar reaction between Ru( $C \equiv CC \equiv C-Li$ ) (dppe)Cp\* and *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> afforded {Cp\*(dppe)Ru}C  $\equiv$ CC  $\equiv$ C{*trans*-PtCl(PPh<sub>3</sub>)<sub>2</sub>} **15** in 40% yield. Spectroscopic data include a broad resonance between  $\delta$  6.83–8.02 arising from the ten Ph groups, while the <sup>31</sup>P NMR spectrum contains two equal intensity resonances at  $\delta_P$  81.9 (dppe) and 22.2 (PPh<sub>3</sub>); the Pt satellites of the latter resonance were not resolved.

The ES-MS contained  $M^+$  at m/z 1437. No other tractable products were obtained.

(c) {*CuCl(PPh<sub>3</sub>)*}<sub>4</sub>. Extending the synthetic route to other Group 11 metals, the reaction between Ru( $C \equiv CC \equiv CLi$ )(dppe)Cp<sup>\*</sup> and {CuCl(PPh<sub>3</sub>)}<sub>4</sub> was found to give the Ru<sub>2</sub>C<sub>8</sub> complex, {Ru(dppe) Cp<sup>\*</sup>}<sub>2</sub>( $\mu$ - $C \equiv CC \equiv CC \equiv CC \equiv C$ ) **16**, in 85% yield. Characterisation of this complex was from microanalysis and spectroscopic data, including IR [ $\nu$ ( $C \equiv C$ ) at 1949, 2101 cm<sup>-1</sup>] and M<sup>+</sup> at *m*/*z* 1366 in the ES-MS, together with an XRD molecular structure determination which has been reported previously on another occasion. In all cases, the data are identical with those obtained from an authentic sample [26].

While the exact mechanism of formation of this copper-free derivative was not determined, a likely route involves the oxidative coupling of the lithio reagent, possibly via a radical intermediate. Previous syntheses of binuclear  $C_8$  complexes have proceeded from either the chloro-metal complex and Me<sub>3</sub>Si(C=C)<sub>4</sub>SiMe<sub>3</sub> in the presence of KF and wet MeOH, or by oxidative coupling of Ru(C=CC=CH)(dppe)Cp\* [with Cul/tmeda; Hay conditions] [26].

(d)  $(AuCl)_2(\mu$ -dppm). We have previously described the synthesis of  $\{Au(C \equiv CC \equiv CH)\}_2(\mu - dppm)$  from  $(AuCl)_2(\mu - dppm)$ and HC≡CC≡CH under Cadiot-Chodkiewicz conditions. while the tetrametallic derivative {Cp(OC)<sub>3</sub>WC $\equiv$ CC $\equiv$ CAu}<sub>2</sub>( $\mu$ -dppm) was similarly formed from W(C $\equiv$ CC $\equiv$ CH)(CO)<sub>3</sub>Cp and (AuCl)<sub>2</sub>( $\mu$ dppm) [27]. The related ruthenium complex {Cp\*(dppe)  $RuC \equiv CC \equiv CAu_{2}(\mu-dppm)$  17 could not be prepared in this manner. However, addition of  $(AuCl)_2(\mu$ -dppm) to two equiv. Ru(C=CC=CLi)(dppe)Cp\* generated in thf in situ afforded 17 in 90% yield. Characterisation followed from IR [ $\nu$ (C=C) at 1982, 2106 cm<sup>-1</sup>], <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (particularly two resonances at  $\delta_P$  82.0, 35.6, relative intensities 2:2, assigned to dppe and dppm ligands, respectively). The <sup>13</sup>C NMR spectrum contains resonances assigned to the Cp\*, dppm and dppe ligands, but none of the C<sub>4</sub> chain signals were found. The ES-MS contains  $[M-H]^+$  at m/z 2143. Although  $\{Au(C \equiv CBu^t)\}_2(\mu$ -dppm) has a U-



**Fig. 1.** Plot of the molecule of **8** projected onto the plane of the Cp\* ring, showing atom numbering scheme.



Fig. 2. Plot of the molecule of 13 projected onto the plane of the Cp\* ring, showing atom numbering scheme.

shaped geometry [28], it is likely that the steric bulk of the Ru(dppe)Cp\* fragments precludes this geometry for **17**.

- 2.5. Reactions of Ru(C=CC=CLi)(PPh<sub>3</sub>)<sub>2</sub>Cp
- (a) *trans-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>*. The complex {Cp(PPh<sub>3</sub>)<sub>2</sub>Ru}(C=CC=C) {Rh(CO)(PPh<sub>3</sub>)<sub>2</sub>} **18** was obtained from the reaction of Ru(C=CC=CH)(PPh<sub>3</sub>)<sub>2</sub>Cp treated with *n*-BuLi at  $-78 \degree$ C, followed by addition of one equivalent of *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>. Complex **18** displayed all expected resonances in the <sup>1</sup>H, <sup>31</sup>P NMR analysis, IR, microanalysis and ES-MS. In the <sup>1</sup>H and <sup>31</sup>P NMR spectra, the characteristic peaks for the Ru(PPh<sub>3</sub>)<sub>2</sub>Cp and Rh(CO)(PPh<sub>3</sub>)<sub>2</sub> groups are present, the PPh<sub>3</sub> ligands being distinguished in the <sup>31</sup>P NMR spectrum by resonances at  $\delta_P$  38.5 (Rh) and 50.6 (Ru). In the IR spectrum, two  $\nu$ (C=C) bands at 1978 and 1955 cm<sup>-1</sup> and one  $\nu$ (CO) band at 2108 cm<sup>-1</sup> were observed. The ES-MS of **18** contains M<sup>+</sup> at *m/z* 1394 and fragment ions at *m/z* 429 and 691 for [Ru(PPh<sub>3</sub>)<sub>n</sub>Cp]<sup>+</sup> (*n* = 1, 2, respectively).
- (b) {*CuCl*(*PPh*<sub>3</sub>)}<sub>4</sub> Lithiation of Ru(C=CC=CH)(PPh<sub>3</sub>)<sub>2</sub>Cp **2** and addition of {CuCl(PPh<sub>3</sub>)}<sub>4</sub> afforded {Cp(Ph<sub>3</sub>P)<sub>2</sub>Ru}C=CC=C {Cu(PPh<sub>3</sub>)} **19**, characterised by elemental microanalysis, the IR, <sup>1</sup>H and <sup>31</sup>P NMR spectra (particularly in the latter, with 2:1 resonances at  $\delta_P$  38.5 and 50.8, assigned to the Cu–PPh<sub>3</sub> and Ru–PPh<sub>3</sub> ligands, respectively) and [M + MeOH]<sup>+</sup> at *m*/*z* 1096 in the ES-MS.

# 2.6. Molecular structures

The molecular structures of **8** and **13** have been determined from single-crystal X-ray diffraction studies with plots of single molecules of each complex being given in Figs. 1 and 2, respectively, non-hydrogen atoms being drawn with 50% probability ellipsoids. Selected bond parameters are listed in Table 2. Structural parameters are similar to those found in many other compounds containing the distorted octahedral Ru(dppe)Cp\* fragment [Ru–P(1,2) 2.2616(6)–2.2778(7), Ru–C(cp) (av.) 2.26 Å], while the diynyl ligand has the expected short–long–short C–C bond alternation [(values for **8/13**) Ru–C(1) 2.038(2)/1.975(3); C(1)–C(2) 1.150(3)/ 1.224(3); C(2)–C(3) 1.428(3)/1.377(3); C(3)–C(4) 1.192(3)/1.209(3), C(4)–C(5) (**8**)/C(4)–Ge (**13**) 1.474(3)/1.881(3) Å]. Angles at Ru confirm the near octahedral distribution of ligands [P(1)–Ru–P(2) 82.57(2)/82.73(2), P(1,2)–Ru–C(1) 79.23(7)–89.02(7)°] while the C<sub>4</sub> chain is close to linear [Ru–C(1)–C(2) 178.11(18)/176.5(2); C(1)–C(2)–C(3) 173.7(2)/176.2(3); C(2)–C(3)–C(4) 177.8(2)/179.0(3); C(3)–C(4)–X [X=C(5) (**8**)/Ge(1) (**13**) 176.5(3)/165.5(2)°]. Interestingly, there appears to be significantly greater degree of delocalisation along the Ru–C<sub>4</sub>–Ge chains than found for the analogous Ru–C<sub>4</sub>–Me derivative.

# 3. Conclusions

The reactions described above (summarised in Schemes 1–3) show that the lithiated metalla-diyne Ru( $C \equiv CC \equiv CLi$ )(dppe)Cp\* **3** is a powerful nucleophilic reagent suitable for preparing a wide range of diynyl complexes containing either functional organic groups or other metal-ligand groups. Some of the products can be obtained from the parent diynes, or by transformation of other functional diynyl complexes, but most are new compounds which have not been obtained by more usual approaches. The difference in reactivity of the two lithiated intermediates with {CuCl(PPh<sub>3</sub>)}<sub>4</sub> may be the result of oxidation of the more electrophilic Ru(dppe) Cp\* derivative; at this time, we have not pursued this matter further.

We note that attack at the CO group does not occur in the reactions which afford **9**, **10** and **11**, thus (under these conditions at least) precluding access to complexes containing longer carbon chains into which a CR group has been formally inserted. Similarly, in the reaction with *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, there was no evidence for the replacement of the second Cl atom to form disubstituted complex, which would have contained an interesting Ru–C<sub>4</sub>–Pt–C<sub>4</sub>–Ru array. Further work on compounds of these types will be presented elsewhere.

The new compounds are characterised spectroscopically, all showing the expected IR absorptions or NMR resonances, while the ES-MS contain molecular ions, or adducts with solvent or other ions present. Common features include the  $[Ru(PPh_3)_nCp]^+$  (n = 1, 2) ions (at m/z 429 and 635, respectively) or  $[Ru(dppe)Cp^*]^+$  at m/z 651. The molecular structures of two examples (**8** and **13**) have been confirmed by single-crystal XRD structure determinations, from which it is apparent that replacement of Me (in **8**) by GePh<sub>3</sub> (in **13**) results in some delocalisation along the C<sub>4</sub> chain.

#### 4. Experimental

#### 4.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates  $(20 \times 20 \text{ cm}^2)$  coated with silica gel (Merck, 0.5 mm thick).

#### 4.2. Instruments

IR spectra: Bruker IFS28 FT-IR spectrometer. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra: Varian 2000 instrument (<sup>1</sup>H at 300.13 MHz, <sup>13</sup>C at 75.47 MHz, <sup>31</sup>P at 121.503 MHz) at 298 K. Samples were dissolved in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C NMR spectra and external H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR spectra. Electrospray mass spectra (ES MS; positive-ion mode): Fisons Platform II spectrometer. Solutions in MeOH or MeCN were injected into a via a 10 ml injection loop; nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used as required [29]. Elemental analyses were by CMAS, Belmont, Vic. 3216, Australia.

#### 4.3. Reagents

Ru(C=CC=CH)(PP)Cp' [(PP)Cp' = (PPh\_3)\_2Cp, (dppe)Cp\* [24]], (AuCl)<sub>2</sub>( $\mu$ -dppm) [28,30], *trans*-RhCl(CO)(PPh\_3)<sub>2</sub> [31], *cis*-PtCl<sub>2</sub>(PPh\_3)<sub>2</sub> [32], {CuCl(PPh\_3)}<sub>4</sub> [33] and AuCl(PPh\_3) [34] were prepared as previously described. Organolithium reagents [LiMe.-LiBr, 1.5 M solution in Et<sub>2</sub>O; LiBu, 1.6 M or 2.3 M solutions in hexanes, or 1.045 M solution in thf; LiBu<sup>t</sup>, 1.6 M solution in heptane] were obtained from Aldrich; LDA was made from LiBu in hexanes and NHMe<sub>2</sub>. Other reagents were commercial samples from Aldrich or Fluka and were used as received.

# 4.4. Lithiation experiments

- (a) SiClMe<sub>3</sub>.
- (i) A solution of Ru(C=CC=CH)(dppe)Cp\* **1** (50 mg, 0.07 mmol) in thf (5 ml) was treated with LiBu (140 µl, 1.045 M solution in thf) at -78 °C and stirrred for 30 min. An aliquot of SiClMe<sub>3</sub> (18 ml, 0.14 mmol) was added and the reaction mixture was allowed to warm to r.t. over 2 h. Solvent was removed to give a yellow residue which was then dissolved in hexane (70 ml), filtered via cannula and evaporated to dryness to give Ru(C=CC=CSiMe<sub>3</sub>)(dppe)Cp\* **4** (47 mg, 86%) as a bright yellow powder, identified by comparison with literature data. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.29 (s, 9H, SiMe<sub>3</sub>), 1.56 (s, 15H, Cp\*), 1.81–1.88, 2.52–2.56 (2 × m, 2 ×v2H, dppe-CH<sub>2</sub>), 7.02–7.87 (m, 20H, Ph). <sup>31</sup>P NMR:  $\delta$  81.3 (s, dppe). Lit. values [24]: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.23, 1.53, 1.78–2.49 (2 × m), 6.89–7.86. <sup>31</sup>P NMR:  $\delta$  81.3.
- (ii) Similarly, from Ru(C≡CC≡CH)(PPh<sub>3</sub>)<sub>2</sub>Cp 2 (51 mg, 0.07 mmol) and SiClMe<sub>3</sub> (17 ml, 0.14 mmol) was obtained Ru(C≡CC≡CSiMe<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cp 5 (45mg, 80%) as a bright yellow powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.28 (s, 9H, SiMe<sub>3</sub>), 4.36 (s, 5H, Cp), 6.91–7.59 (m, 30H, Ph). <sup>31</sup>P NMR: δ 50.8 (s, PPh<sub>3</sub>). Lit. values [24]: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.26, 4.30, 6.92–7.58. <sup>31</sup>P NMR: δ 50.7.

(b) AuCl(PPh<sub>3</sub>).

- (i) Similar lithiation of Ru(C=CC=CH)(dppe)Cp\* (51 mg, 0.07 mmol) and treatment with AuCl(PPh<sub>3</sub>) (39 mg, 0.07 mmol) afforded bright yellow Ru{C=CC=CAu(PPh<sub>3</sub>)} (dppe)Cp\* **6** (72 mg, 85%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.54 (s, 15H, Cp\*), 2.14–2.20, 2.73–2.76 (2 × m, 2 × 2H, dppe-CH<sub>2</sub>), 6.96–7.86 (m, 35H, Ph). Lit. values [24]:  $\nu$ (C=C) 2119m, 2072m, 1981w cm<sup>-1</sup>;  $\delta$ <sub>H</sub> 1.52 (Cp\*).
- (ii) Similarly, lithiated Ru(C=CC=CH)(PPh<sub>3</sub>)<sub>2</sub>Cp (51 mg, 0.07 mmol) and AuCl(PPh<sub>3</sub>) (68 mg, 0.14 mmol) gave bright yellow Ru{C=CC=CAu(PPh<sub>3</sub>)}(PPh<sub>3</sub>)<sub>2</sub>Cp 7 (57 mg, 70%). IR (Nujol)/cm<sup>-1</sup>: v(C=C) 1983m, 2073m. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.40 (s, 5H, Cp), 6.86–7.64 (m, 45H, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 33.9 (s, 1P, Au-PPh<sub>3</sub>), 51.2 (s, 2P, Ru-PPh<sub>3</sub>). Lit. values [24]: IR/cm<sup>-1</sup>: v(C=C) 2116m, 2073m, 1982m cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.28, 7.08–7.59. <sup>31</sup>P NMR: δ 32.5, 49.9.

4.5. Reactions of  $Ru(C \equiv CC \equiv CLi)(dppe)Cp^*$  **3** with organic electrophiles

(a) Mel. A solution of Ru(C=CC=CH)(dppe)Cp\* (50 mg, 0.07 mmol) in thf (5 ml) at -78 °C was treated with LiBu (91 μl, 1.6 M solution in hexanes). After stirring for 30 min, Mel (32 μl, 0.51 mmol) was added and the mixture was allowed to warm to r.t. over 3 h. Removal of solvent, extraction with hexane (60 ml), filtration via cannula and evaporation to dryness gave Ru(C=CC=CMe)(dppe)Cp\* 8 (40 mg, 70%) as a bright yellow powder. Single crystals suitable for the X-ray study were

obtained from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Anal. Calcd (C<sub>41</sub>H<sub>42</sub>P<sub>2</sub>Ru): C, 70.47; H, 6.06; *M*, 700. Found: C, 70.45; H, 5.99. IR (CH<sub>2</sub>Cl<sub>2</sub>)/ cm<sup>-1</sup>:  $\nu$ (C=C) 1908m, 2029m. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.60 (s, 15H, Cp\*), 1.73 (s, 3H, Me), 1.87–2.01, 2.62–2.65 (2 × m, 2 × 2H, dppe), 6.89–7.28 (m, 20H, Ph). <sup>13</sup>C NMR:  $\delta$  10.12 (C<sub>5</sub>*Me*<sub>5</sub>), 21.03 (Me), 29.27–29.88 (m, CH<sub>2</sub>), 93.25 (C<sub>5</sub>Me<sub>5</sub>), 52.46, 76.86, 91.73, 124.69 [4 × s, C(4), C(3), C(2), C(1)], 127.42–133.96 (m, Ph). <sup>31</sup>P NMR:  $\delta$  81.6 (s, dppe). ES-MS (MeOH)/*m*/*z*: 731, [M + MeOH]<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.

- (b) *MeC(O)Cl.* From a similar reaction using Ru( $C \equiv CC \equiv CH$ )(dppe) Cp\* (50 mg, 0.07 mmol), LiBu (64 µl, 2.3 M solution in hexanes) and acetyl chloride (26 µl, 0.36 mmol), addition of hexane (20 ml) dropwise to the reaction mixture afforded Ru { $C \equiv CC \equiv CC(O)Me$ }(dppe)Cp\* **9** (34 mg, 60%) as a bright yellow crystalline powder. Anal. Calcd (C<sub>42</sub>H<sub>42</sub>OP<sub>2</sub>Ru): C, 69.40; H, 5.83; *M*, 725. Found: C, 69.36; H, 5.92. IR (Nujol)/cm<sup>-1</sup>:  $\nu(C \equiv C)$ 2004m, 2048m;  $\nu(CO)$  1710m. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.58 (s, 15H, Cp\*), 2.14 (s, 3H, Me), 1.78–1.85, 2.61–2.68 (2 × m, 2 × 2H, dppe), 7.02–7.23 (m, 20H, Ph). <sup>13</sup>C NMR:  $\delta$  10.83 (C<sub>5</sub>Me<sub>5</sub>), 30.13–30.83 (m, dppe), 33.35 (s, Me), 94.38 (C<sub>5</sub>Me<sub>5</sub>), 90.15, 102.13, 118.52, 121.86 [4 × s, C(4), C(3), C(2), C(1)], 126.96–134.51 (m, Ph), 201.57 (CO). <sup>31</sup>P NMR:  $\delta$  81.7 (s, dppe). ES-MS (MeOH)/*m*/*z*: 725, M<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.
- (c) *PhC(O)Cl.* Similarly, Ru( $C \equiv CC \equiv CH$ )(dppe)Cp\* (50 mg, 0.07 mmol), benzoyl chloride (17 µl, 0.14 mmol) gave Ru { $C \equiv CC \equiv CC(O)Ph$ }(dppe)Cp\* **10** as a red powder (43 mg, 75%). Anal. Calcd (C<sub>47</sub>H<sub>44</sub>OP<sub>2</sub>Ru): C, 71.65; H, 5.63; *M*, 788. Found: C, 71.76; H, 5.60. IR (Nujol)/cm<sup>-1</sup>:  $\nu$ ( $C \equiv C$ ) 2000m, 2109m;  $\nu$ (CO) 1716m. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.51 (s, 15H, Cp\*), 2.08–2.18, 2.50–2.54 (2 × m, 2 × 2H, dppe), 7.05–7.28 (m, 25H, Ph). <sup>13</sup>C NMR:  $\delta$  10.02 (s, C<sub>5</sub>Me<sub>5</sub>), 29.23–30.12 (m, dppe), 94.13 [t, *J*(CP) = 2 Hz, C<sub>5</sub>Me<sub>5</sub>], 63.08, 95.59, 101.00, 112.17 [4 × s, C(4), C(3), C(2), C(1)], 127.63–133.63 (m, Ph), 206.41 (s, CO). <sup>31</sup>P NMR:  $\delta$  80.5 (s, dppe). ES-MS (MeOH)/*m*/*z*: 811, [M + Na]<sup>+</sup>; 788, M<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.
- (d) *ClC(O)OMe*. Similarly, from Ru(C=CC=CH)(dppe)Cp\* (51 mg, 0.07 mmol) and methyl chloroformate (12 µl, 0.15 mmol) was obtained Ru{C=CC=CC(O)OMe}(dppe)Cp\* **11** (20 mg, 40%) as a yellow powder. IR (Nujol)/cm<sup>-1</sup>:  $\nu$ (C=C) 1971m, 2008m;  $\nu$ (CO) 1723m. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.53 (s, 15H, Cp\*), 1.68 (s, 3H, Me), 2.06–2.13, 2.38–2.43 (2 × m, 2 × 2H, dppe), 7.02–7.26 (m, 20H, Ph). <sup>31</sup>P NMR:  $\delta$  80.6 (s, dppe). ES-MS (MeOH)/*m*/*z*: 743, M<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>. No satisfactory microanalysis or <sup>13</sup>C NMR spectrum could be obtained for this unstable complex.
- (e) *PhCHO*. Benzaldehyde (15 µl, 0.14 mmol) was added to lithiated Ru(C=CC=CH)(dppe)Cp\* (50 mg, 0.07 mmol) in thf (5 ml) and the mixture was stirred for 30 min. Addition of water (1 ml), warming to r.t. over 2 h and removal of solvent gave a yellow residue. Extraction with hexane (60 ml), filtration via cannula and evaporation afforded Ru{C=CC=CCHPh(OH)}(dppe)Cp\* **12** (44 mg, 76%) as a bright orange crystalline powder. Anal. Calcd  $(C_{47}H_{46}OP_2Ru)$ : c, 71.37; H, 5.87; *M*, 790. Found: C, 70.92; H, 5.87. IR (Nujol)/cm<sup>-1</sup>:  $\nu$ (OH) 3303w,  $\nu$ (C=C) 2000m, 2106m. <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  1.57 (s, 15H, Cp\*), 1.66 (s, 1H, CH), 1.74–1.80, 2.56–2.58 (2 × s, 2 × 2H, dppe), 5.52 (s, 1H, OH), 7.03–7.29 (m, 25H, Ph). <sup>13</sup>C NMR:  $\delta$  10.07 (s,  $C_5Me_5$ ), 29.29–29.90 (m, dppe), 79.89 (s, CH), 93.24 (s br,  $C_5Me_5$ ), 65.85, 88.72, 99.22, 122.10 [4s, C(4), C(3), C(2), C(1)], 127.68–133.74 (m, Ph). <sup>31</sup>P NMR:  $\delta$  81.3 (s, dppe). ES-MS (MeOH)/*m*/*z*: 813, [M + Na]<sup>+</sup>; 790, M<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.

4.6. Reactions of  $Ru(C \equiv CC \equiv CLi)(dppe)Cp^*$  with metal halides

(a) GeClPh<sub>3</sub>. A solution of Ru(C=CC=CH)(dppe)Cp\* **1** (50 mg, 0.07 mmol) in thf (5 ml) was treated with LiBu (50  $\mu$ l, 2.3 M

solution in hexanes) at -78 °C and stirred for 30 min. GeClPh<sub>3</sub> (31 mg, 0.07 mmol) was added and the mixture was allowed to warm to r.t. over 3 h. Solvent was removed and the yellow residue was extracted with hexane (60 ml) and filtered via cannula. Removal of solvent from the filtrate gave  $Ru(C \equiv CC \equiv CGePh_3)(dppe)Cp^*$  **13** (62 mg, 82%) as a yellow crystalline powder. Single crystals suitable for X-ray studies were grown from thf/hexane. Anal. Calcd (C<sub>58</sub>H<sub>54</sub>GeP<sub>2</sub>Ru): C, 70.60; H, 5.52; M, 987. Found: C, 70.61; H, 5.55. IR (Nujol)/ cm<sup>-1</sup>: ν(C=C) 2000m, 2106m. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.56 (s, 15H, Cp\*), 1.75–1.792.50–2.53 (2 × m, 2 × 2H, dppe-CH<sub>2</sub>), 6.89–7.85 (m, 35H, Ph). <sup>13</sup>C NMR:  $\delta$  10.17 (s, C<sub>5</sub>Me<sub>5</sub>), 29.62–30.12 (dppe-CH<sub>2</sub>), 93.22 (C<sub>5</sub>Me<sub>5</sub>), 62.40, 86.85, 93.46, 99.42 [4 × s, C(4), C(3), C(2), C(1)], 127.64–137.76 (m, Ph). <sup>31</sup>P NMR: δ 81.0 (s, dppe). ES-MS (MeCN)/m/z: 1009, [M + Na]+; 988, [M + H]<sup>+</sup>; 675, [Ru(N-CMe)(dppe)Cp\*]<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.

- (b) *SnClPh*<sub>3</sub>. Similarly, from Ru(C=CC=CH)(dppe)Cp<sup>\*</sup> (50 mg, 0.07 mmol) and SnClPh<sub>3</sub> (45 mg, 0.11 mmol) was obtained Ru(C=CC=CSnPh<sub>3</sub>)(dppe)Cp<sup>\*</sup> **14** (54 mg, 70%) as a yellow crystalline powder. Anal. Calcd ( $C_{58}H_{54}P_2RuSn$ ): C, 67.45; H, 5.27; *M*, 1033. Found: C, 67.97; H, 5.51. IR (Nujol)/cm<sup>-1</sup>:  $\nu$ (C=C) 1977m, 2081m. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.56 (s, 15H, Cp<sup>\*</sup>), 1.78–1.81, 2.52–2.55 (2 × m, 2 × 2H, dppe-CH<sub>2</sub>), 7.01–7.89 (m, 35H, Ph). <sup>13</sup>C NMR:  $\delta$  10.21 (s, C<sub>5</sub>*Me*<sub>5</sub>), 29.86–30.01 (m, dppe-CH<sub>2</sub>), 91.87 (s, C<sub>5</sub>Me<sub>5</sub>), 74.82, 86.85, 99.05, 103.22 [4 × s, C(4), C(3), C(2), C(1)], 127.84–134.02 (m, Ph). <sup>31</sup>P NMR:  $\delta$  81.2 (s, dppe). ES-MS (MeCN)/*m*/*z*: 1033, M<sup>+</sup>; 675, [Ru(NCMe)(dppe)Cp<sup>\*</sup>]<sup>+</sup>; 635, [Ru(dppe)Cp<sup>\*</sup>]<sup>+</sup>.
- (c) *cis-PtCl*<sub>2</sub>(*PPh*<sub>3</sub>)<sub>2</sub>. Similarly, the reaction of lithiated Ru(C=CC=CH)(dppe)Cp\* (50 mg, 0.07 mmol) and *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (59 mg, 0.07 mmol) gave {Cp\*(dppe)Ru}C=CC=C {PtCl(PPh<sub>3</sub>)<sub>2</sub>-*trans*} **15** (43 mg, 40%) as a bright yellow powder. Anal. Calcd (C<sub>76</sub>H<sub>69</sub>ClP<sub>4</sub>PtRu): C, 63.48; H, 4.84; *M*, 1437. Found: C, 63.60; H, 5.81. IR (Nujol)/cm<sup>-1</sup>:  $\nu$ (C=C) 1984m, 2105m. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.54(s, 15H, Cp\*), 1.84–1.90 (2 × m, 2 × 2H, dppe-CH<sub>2</sub>), 6.83–8.02 (m, 50H, Ph). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  22.2 (s, 2P, Pt-PPh<sub>3</sub>), 81.9 (s, 2P, Ru-dppe). ES-MS (MeOH)/*m*/*z*: 1437, M<sup>+</sup>; 1436, [M H]<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.
- (d) {*CuCl*(*PPh*<sub>3</sub>)}<sub>4</sub>. A solution of Ru(C=CC=CH)(dppe)Cp\* **1** (51 mg, 0.07 mmol) in thf (2 ml) was treated with LiBu (140 µl, 1.045 M solution in thf) at -78 °C and stirred for 30 min. A solution of {*CuCl*(PPh<sub>3</sub>)}<sub>4</sub> (28 mg, 0.07 mmol) in thf (5 ml) was then added via cannula and the mixture was allowed to warm to r.t. over 3 h. The resulting red-orange precipitate was collected and washed with hexane to give {Ru(dppe)Cp\*}<sub>2</sub>( $\mu$ -C=CC=CC=CC=C) **16** (86 mg, 85%). Single crystals suitable for an X-ray study were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane. The compound was also identified by comparison with an authentic sample [27].
- (e)  $(AuCl)_2(\mu$ -dppm). A solution of Ru(C=CC=CH)(dppe)Cp\* (100 mg, 0.15 mmol) in thf (5 ml) was treated with LiBu  $(140 \mu l,$ 1.045 M solution in thf) at -78 °C and stirred for 1 h. (AuCl)<sub>2</sub>( $\mu$ dppm) (60 mg, 0.07 mmol) was added and the resulting yellow precipitate was collected, washed with hexane and dried to give {Au(C=CC=C [Ru(dppe)Cp\*])}<sub>2</sub>( $\mu$ -dppm) **17** (135 mg, 90%). Anal. Calcd (C<sub>105</sub>H<sub>100</sub>Au<sub>2</sub>P<sub>6</sub>Ru<sub>2</sub>): C, 58.83; H, 4.70; M, 2144. Found: C, 58.88; H, 4.75. IR (Nujol)/cm<sup>-1</sup>: ν(C≡C) 982m, 2106m. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  1.56 (s,  $Cp^*$ ), 1.81–1.92, 2.80–2.89 (2 × m, 2 × 2H, dppe-CH<sub>2</sub>), 3.23 (s, 2H, dppm-CH<sub>2</sub>), 6.85–7.97 (m, 60H, Ph). <sup>13</sup>C NMR:  $\delta$  10.08 (C<sub>5</sub>Me<sub>5</sub>), 29.86–30.12 (dppe-CH<sub>2</sub>), 43.33 (dppm-CH<sub>2</sub>), 93.12 (C<sub>5</sub>Me<sub>5</sub>), 127.64–133.76 (m, Ph). <sup>31</sup>P NMR: δ 35.6 (s, 2P, dppm), 82.0 (s, 2P, dppe). ES-MS (MeCN)/ m/z: 2143,  $[M - H]^+$ ; 1460,  $[M - C_4Ru(dppe)Cp^*]^+$ ; 1366,  $[M - Au_2(dppm)]^+$ ; 675,  $[Ru(NCMe)(dppe)Cp^*]^+$ ; 635.  $[Ru(dppe)Cp^*]^+$ .

- 4.7. Reactions of Ru(C=CC=CLi)(PPh<sub>3</sub>)<sub>2</sub>Cp
- (a) *trans-RhCl(CO)(PPh<sub>3</sub>)*<sub>2</sub>. Similarly, {Cp(PPh<sub>3</sub>)<sub>2</sub>Ru}(C=CC=C) {Rh(CO)(PPh<sub>3</sub>)<sub>2</sub>} **18** was obtained as a yellow powder (49 mg, 50%) from the reaction between lithiated Ru(C=CC=CH) (PPh<sub>3</sub>)<sub>2</sub>Cp (53 mg, 0.07 mmol) and *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> (49 mg, 0.07 mmol). Anal. Calcd. ( $C_{82}H_{65}OP_4RhRu$ ): C, 70.64; H, 4.70. Found: C, 70.73; H, 4.76. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C=C) 2108 (m),  $\nu$ (CO) 1978 (m), 1955 (m). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.17–6.92 (m, 60H, Ph); 4.35 (s, 5H, Cp). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  50.6 (s, Ru(PPh<sub>3</sub>)<sub>2</sub>), 38.5 (s, Rh(PPh<sub>3</sub>)<sub>2</sub>). ES-MS (MeOH)/*m*/*z*: 1394, M<sup>+</sup>; 691, [Ru(PPh<sub>3</sub>)<sub>2</sub>Cp]<sup>+</sup>; 429, [Ru(PPh<sub>3</sub>)Cp]<sup>+</sup>.
- (b) { $CuCl(PPh_3)$ }<sub>4</sub>. A solution of Ru(C=CC=CH)(PPh\_3)<sub>2</sub>Cp **2** (52 mg, 0.07 mmol) in thf (10 ml) was treated with LiBu (140 µl, 1.045 M solution in thf) for 30 min at -78 °C. { $CuCl(PPh_3)$ }<sub>4</sub> (25 mg, 0.07 mmol) was then added and the mixture was allowed to warm to r.t. over 2 h. Solvent was removed and the residue was dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and purified by column chromatography (basic alumina, acetone-hexane 3/7). A yellow fraction contained { $Cp(Ph_3P)_2Ru$ }C=CC=C{ $Cu(PPh_3)$ } **19** (30 mg, 40%). Anal. Calcd ( $C_{63}H_{50}CuP_3Ru$ ): C, 71.04; H, 4.74; *M*, 1065. Found: C, 71.08; H, 4.79. IR (CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup>:  $\nu$ (C=C) 1994m, 2106m. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  4.24 (s, 5H, Cp), 6.89–7.76 (m, 45H, Ph). <sup>31</sup>P NMR:  $\delta$  50.8 (s, 2P, Ru–PPh<sub>3</sub>), 38.5 (s, 1P, Cu–PPh<sub>3</sub>). ES-MS (MeOH)/*m*/*z*: 1096, [M + MeOH]<sup>+</sup>; 691, [Ru(PPh\_3)<sub>2</sub>Cp]<sup>+</sup>; 429, [Ru(PPh\_3)Cp]<sup>+</sup>.

#### 4.8. Structure determinations

Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer with monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å.  $N_{tot}$  reflections were merged to N unique ( $R_{int}$  cited) after multiscan absorption correction (proprietary software),  $N_0$  with  $I > 2\sigma(I)$ . The structures were refined against  $F^2$  with full-matrix least-squares using the program SHELXL-97 [35]. All H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the isotropic displacement parameter of the parent atom. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. Conventional residuals R1, wR2 on  $|F^2|$  are quoted. Neutral atom complex scattering factors were used.

**8** Ru(C=CC=CMe)(dppe)Cp\* =  $C_{41}H_{42}P_2$ Ru, M = 697.8. Monoclinic, space group  $P_{2_1}/n$ , a = 16.615(2), b = 10.4210(7), c = 21.115(2) Å,  $\beta = 111.863(9)^\circ$ , V = 3393.0(6) Å<sup>3</sup>,  $D_c = 1.366$  g cm<sup>-3</sup>,  $Z = 4.2\theta_{max} = 64^\circ$ ,  $\mu = 0.58$  mm<sup>-1</sup>,  $T_{min/max} = 0.70/0.89$ . Crystal 0.40 × 0.20 × 0.20 mm.  $N_{tot} = 41545$ , N = 10687 ( $R_{int} = 0.035$ ),  $N_o = 8049$ , R1 = 0.037, wR2 = 0.100 [ $I > 2\sigma(I)$ ]; R1 = 0.049, wR2 = 0.103 (all data).

**13** Ru(C=CC=CGePh<sub>3</sub>)(dppe)Cp<sup>\*</sup> =  $C_{58}H_{54}$ GeP<sub>2</sub>Ru, M = 986.6. Monoclinic, space group  $P_{21}/n$ , a = 21.2123(3), b = 9.1713(1), c = 24.8544(4)Å,  $\beta = 93.410(1)^{\circ}$ , V = 4826.7(1)Å<sup>3</sup>,  $D_c = 1.358$ g cm<sup>-3</sup>, Z = 4.  $2\theta_{max} = 68.7^{\circ}$ ,  $\mu = 1.04$  mm<sup>-1</sup>,  $T_{min/max} = 0.89$ . Crystal  $0.25 \times 0.10 \times 0.09$  mm.  $N_{tot} = 177,515$ , N = 19718 ( $R_{int} = 0.101$ ),  $N_0 = 8417$ , R1 = 0.043, wR2 = 0.076 [ $I > 2\sigma(I)$ ], R1 = 0.113, wR2 = 0.094 (all data).

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#### Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 716005 (**8**), 716006 (**13**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or website: http://www.ccdc.cam.ac.uk).

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