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Selective head-to-tail dimerization of phenylacetylene catalyzed by a diruthenium μ-methylene complex

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Dedicated to Pierre Braunstein in honor of his many distinguished contributions to metal cluster chemistry and catalysis.

Abstract

The μ-methylene complex $[Ru_2(\mu\text{-}CH_2)(CO)_4(\mu\text{-}dppm)_2]$ (**1**) in toluene solution at 75 °C is the first known catalyst for the selective dimerization of PhC≡CH or of PhC≡CD to give the head-to-tail dimer PhC≡CC(Ph)=CH_2 or PhC≡CC(Ph)=CD_2 respectively, probably by a mechanism involving alkenyl–alkynyl group coupling at the diruthenium center. After many turnovers, a new diruthenium complex was detected and identified as $[Ru_2\{\mu\text{-}\eta^2\text{-}PhCCH\}(CO)_4(\mu\text{-}dppm)_2]$ (**2**) which was not an active catalyst for the dimerization reaction, and the organic product PhCCMe was also detected at this stage. Complex **2** was prepared more readily by reaction of PhCCH with $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ (**3**) in toluene at 75 °C. The reaction of **1** with a large excess of PhCCH gave further oligomerization and the major products were identified as an octamer and hexamer of PhCCH. Complex **1** was a catalyst for the dimerization of 1-hexyne to a mixture of dimerization products *E*-BuC≡C–CH=CHBu and BuC≡C–C(Bu)=CH_2 in a ratio of about 2:1, and also for polymerization of HCCH, but it failed to react with the alkynes PhCCMe, PhCCPh or 3-hexyne at 75 °C in toluene.

Keywords: Head-to-tail dimerization; Diruthenium complexes; Alkenyl–alkynyl groups

1. Introduction

The development of efficient catalytic systems for the formation of new carbon–carbon bonds is one of the most challenging topics in organic synthesis [1]. The direct coupling of two terminal alkynes to give an enyne is of high interest because enynes exist in nature and may serve as building blocks for natural products or for further structure elaboration [2]. Since the initial discoveries [2,3] that the dimerization of 1-alkynes to enynes with transition metal compounds as catalysts can occur either by alkynyl–vinylidene coupling (Scheme 1) [2,3] or by alkynyl–vinyl coupling (Scheme 2) [3], there has been considerable activity in the study of transition-metal-mediated dimerization of terminal alkynes [4]. Mononuclear ruthenium complexes are useful catalysts since they can show high regio- and stereoselectivity (Table 1), and the mechanisms have been studied in detail [4]. The formation of enynes in most cases was found to occur mostly by head-to-head dimerization of RC≡CH to give *E*- or *Z*-RC≡CCH=CHR via the alkynyl–vinylidene coupling mechanism described in Scheme 1(a) [2–4]. The single known diruthenium complex catalyst is also believed to act by the alkynyl–vinylidene coupling mechanism although involving both metal centers throughout as shown in Scheme 1(b), and it also gives a linear trimer [5]. The *E*- or *Z*-stereochemistry is controlled by the nature of the alkynyl–vinylidene coupling and only one of the possible stereochemistries is shown in each of Scheme 1(a and b). The less common formation of enynes via head-to-tail dimerization of RC≡CH to give RC≡CCR=CH_2 follows the alkynyl–vinyl coupling mechanism illustrated in Scheme 2 [2–4]. Clearly, it is not possible to form the head-to-tail dimer by the vinylidene mechanism of Scheme 1, but Scheme 2 can lead to either

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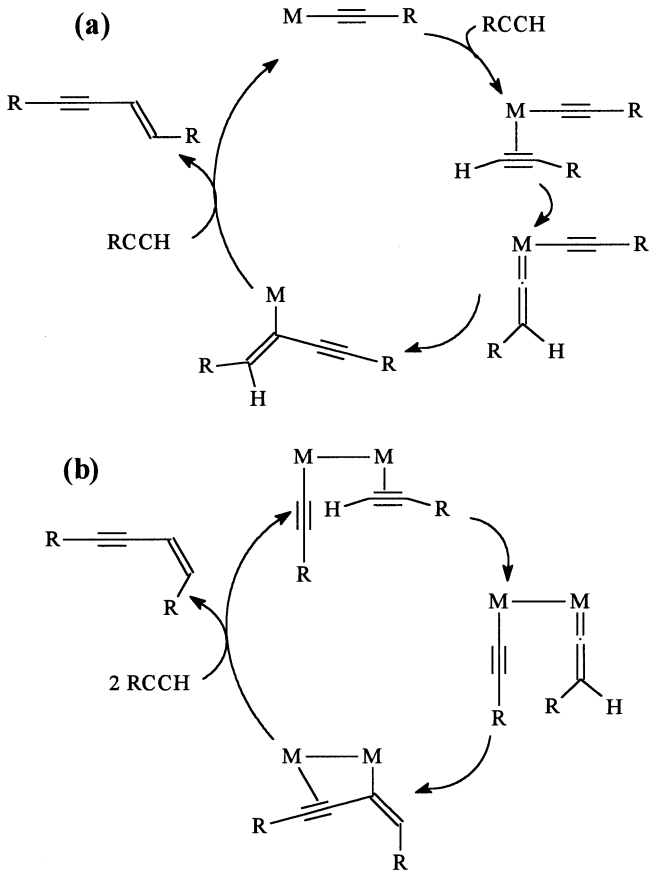
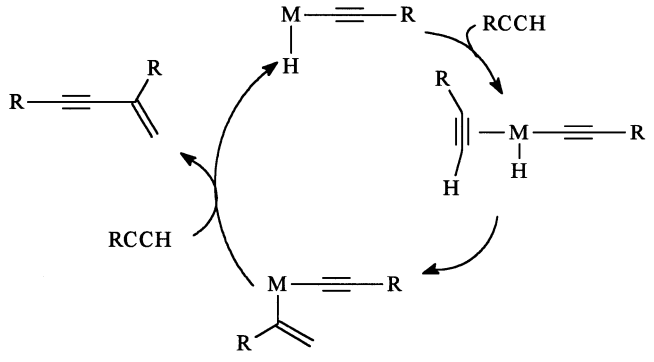


Scheme 1.



Scheme 2.

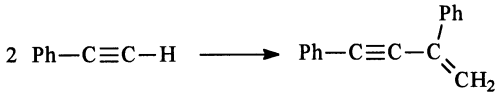
RCCCR=CH_2 or to *E*-RCCCH=CHR, depending on the orientation of the insertion of the alkyne into the MH bond.

As well as this general interest in alkyne dimerization, there has been interest in stoichiometric reactions of alkynes with both mononuclear and binuclear ruthenium complexes. For example, the coupling of alkynes at the diruthenium centers in the μ-methylene complex $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(Cp)_2]$ has been reported [6], while the reactions of alkynes with $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$, dppm = $Ph_2PCH_2PPh_2$, gave alkyne, alkenyl or vinylidene complexes without alkyne coupling [7]. Since the development of binuclear and cluster catalysts remains a considerable challenge [8], it was decided to explore the chemistry of alkynes with the new diruthenium methylene complex $[Ru_2(\mu\text{-}CH_2)(CO)_4(\mu\text{-}dppm)_2]$ [9] and the results are reported below.

2. Results and discussion

2.1. Dimerization of PhC≡CH by $[Ru_2(\mu\text{-}CH_2)(CO)_4(\mu\text{-}dppm)_2]$

At room temperature, the μ-methylene complex $[Ru_2(\mu\text{-}CH_2)(CO)_4(\mu\text{-}dppm)_2]$ (**1**) in toluene solution was inactive toward excess PhC≡CH. However, on warming to 75 °C, the slow formation of 2,4-diphenyl-but-1-en-3-yne, PhC≡CC(Ph)=CH_2, was observed according to Eq. (1), and identified by its NMR spectrum and by GC–MS. Using a molar ratio of PhC≡CH:**1** of 8:1, the conversion of PhC≡CH to PhC≡CC(Ph)=CH_2 was complete within 24 h, with unchanged complex **1** the only ruthenium complex present in detectable quantity, as monitored by ^1H and ^{31}P NMR. The product PhC≡CC(Ph)=CH_2 is formed by the less common head-to-tail dimerization of PhCCH (Schemes 1 and 2), and none of the expected head-to-head dimerization products *E*- or *Z*-PhCCCH=CHPh was detected [2–5].



(1)

At low concentrations of PhCCH, the rate of the catalytic reaction in toluene solution at 75 °C was roughly first order with respect to PhCCH, as shown by data in Table 2, but at higher concentrations there was a saturation effect. After many turnovers, a new diruthenium complex was detected and identified as $[Ru_2\{\mu\text{-}\eta^2\text{-}PhCCH\}(CO)_4(\mu\text{-}dppm)_2]$ (**2**). Complex **2** was not an active catalyst for the dimerization reaction, and so the catalytic activity decreased as **2** was formed from **1**. As complex **2** was formed, the organic product PhCCMe was also detected and identified both by its ^1H NMR spectrum and by GC–MS. The slow formation of **2**, is therefore, described by Eq. (2). Complex **2** was prepared more readily by reaction of $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ (**3**) with PhCCH in toluene at 75 °C, according to Eq. (3). Complex **3** was a poor catalyst for the dimerization of PhCCH under these conditions, and only 5% conversion of PhCCH was observed under conditions where **1** gave 100% conversion

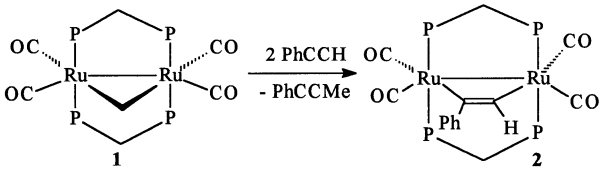
Table 1
Some catalytic systems for the dimerization of 1-alkynes

Catalyst	Monomer	Enyne (yield)	T (°C), time (h), conversion (%)	Reference
$[RhCl(PPh_3)_3]$	1-Hexyne	$BuCC{-}C(Bu){=}CH_2$	20, 30, 64	[2a]
$[RhCl(PPh_3)_3]$	PhCCH	$PhCC{-}C(Ph){=}CH_2$ (14%), PhCC–CH=CHPh (20%)	20, 30, 34	[2a]
[RuHPhL] [a]	PhCCH	PhCC–CH=CHPh, E: 95%, Z: 5%	50, 12, 65	[3e]
RuCp*[C(Cy)NHC=CHN(Cy)]Cl	PhCCH	PhCC–CH=CHPh, E: 76%, Z: 16%, $PhCC{-}C(Ph){=}CH_2$ (8%)	20, 0.05, 100	[4k]
$RuH_2(CO)(PPh_3)_3$	t-BuCCH	t-BuCC–CH=CHBu-t, E: 85%, Z: 15%	100, 10, 51	[3d]
$RuClTp(PPh_3)_2$	PhCCH	PhCC–CH=CHPh, E: 76%, Z: 16%	110, 20, 97	[4d]
$RuCp^*(PPh_3)CCPh$	PhCCH	PhCC–CH=CHPh, E: 80%, Z: 20%	20, 20, 75	[4b]
$Ru_2Cp^*_2(SPr)_2R$ [b]	FcCCH	Z-FcCC–CH=CHFc	60, 30, 62	[5]

[a] $L = P\{(CH_2)_3PMe_2\}_3$.
[b] R = C(=CHFc)CCFc, Fc = ferrocenyl.

Table 2
Catalytic dimerization of PhCCH in the presence of complex **1** (0.0135 mmol) at 75 °C for 24 h

PhC≡CH (mmol)	Monomer conversion (%)	TON
0.11	100	8
0.27	77	15
0.54	69	28
0.90	43	29



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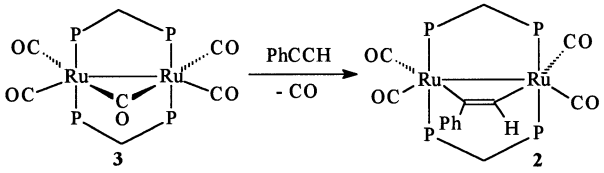


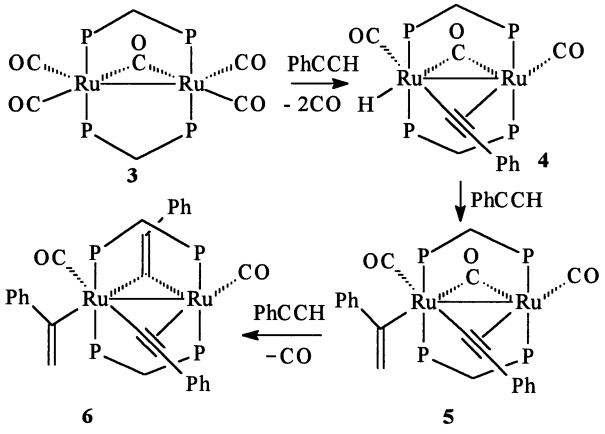
(3)

Complex **2** was characterized by its spectroscopic data, by comparison with the spectra of similar complexes $[Ru_2\{\mu\text{-}\eta^2\text{-}RCCH\}(CO)_4(\mu\text{-}dppm)_2]$, for example, with the analogous complex having $R = CO_2Me$ [7]. The ^{31}P NMR spectrum of complex **2** contained two multiplets centered at $\delta = 32.5$ and 34.5 for the phosphorus atoms of the dppm ligands. The ^1H NMR spectrum exhibited a singlet resonance at $\delta = 8.20$ due to the PhC=CH proton and two multiplets at $\delta = 4.05$ and 2.60 for the CH_2P_2 protons of the dppm ligands. In a ^{13}CO labeled sample of **2**, four terminal carbonyl resonances were observed at $\delta = 218$, 209, 208 and 207 in the ^{13}C NMR spectrum. Consistent with the proposed structure, the IR spectrum showed four terminal CO peaks at 1992, 1988, 1980 and 1950 cm^{-1}, and a peak at 1590 cm^{-1} due to the C=C stretching vibration of the coordinated PhC=CH group.

The corresponding dimerization of PhCCD at 75 °C, with complex **1** as catalyst, was monitored by ^2H NMR, while the ruthenium complexes present were identified by ^{31}P NMR. After 24 h, the enyne $PhCC{-}C(Ph){=}CD_2$ was observed as the only organic product, and **1** was the only ruthenium complex. Over longer reaction periods, the organic product $PhCCCH_2D$ was detected as complex **1** was slowly converted to **2**. Formation of $PhCCCH_2D$ clearly involves combination of PhCCD and CH_2, derived from the μ-methylene group of **1**.

2.2. The mechanism of the dimerization reaction

The observations described above do not define the mechanism of reaction but, in combination with stoichiometric reactions studied previously [7], it is possible to make a reasoned hypothesis. The reaction of complex **3** with PhCCH in more polar solvents acetone or dichloromethane does not occur as shown in Eq. (3), but in the stepwise manner shown in Scheme 3. The first product is the hydrido(μ-alkynyl) complex **4**, which then



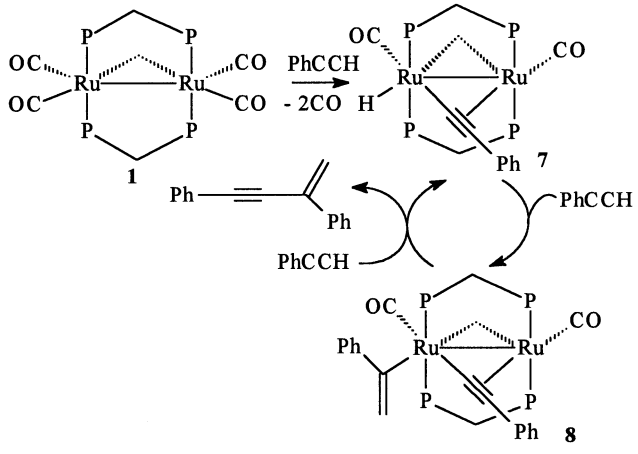
Scheme 3.

reacts with more PhCCH to give the alkenyl(μ-alkynyl) complex **5** and finally the alkenyl(μ-alkynyl)(μ-alkylidene) complex **6**. Coupling of the alkenyl and alkynyl groups in **5** or **6** would give the dimer PhCCC(Ph)=CH_2, and this is probably a key step in the mechanism of dimerization when the catalyst is **3**.

By analogy with Scheme 3, the reaction of PhCCH with complex **1** may occur to give the hydrido(alkynyl)(methylene) complex **7**, and then the alkenyl(μ-alkynyl)(μ-methylene) complex **8** (Scheme 4). The product PhCCC(Ph)=CH_2 is then formed by reductive elimination with coupling of the alkenyl and alkynyl groups, and addition of PhCCH regenerates **7** as shown in Scheme 4. Complex **1** can then be considered as a catalyst precursor to the active complexes **7** and **8** that were not detectable. This proposed mechanism is a binuclear variant of the alkenyl–alkynyl coupling mechanism of Scheme 2. The mechanism of Scheme 1, that has been observed with most other ruthenium-based catalysts [2–5], including the only previous case of a binuclear catalyst [5], is not capable of giving the observed head-to-tail dimer and so can be eliminated.

The termination is likely to occur according to Scheme 5. If the reaction of PhCCH with **1** occurs in such a way that the hydride forms *cis* to the μ-methylene group, as in **9**, then these groups are likely to combine to form a methyl group in complex **10**. Reductive coupling of the methyl and alkynyl groups then forms the organic product PhCCMe, and addition of PhCCH across the Ru–Ru bond occurs to give the inactive complex **2**. Again, neither proposed intermediate **9** or **10** was observed and so the detailed structures are speculative. However, the overall Scheme 5 is fully consistent with the formation of $PhCCCD_2H$ from the μ-CD_2 complex **1**-d_2. It is also noted that reactive methyldiruthenium complexes are known to be formed by reaction of **1** with other protic reagents [9].

Overall, the role of the μ-methylene group in enhancing the catalytic activity is probably in part just to block formation of the inactive μ-alkyne complex **2**. However, the electronic effects could also be important in labilizing carbonyl ligands to generate vacant sites for reactivity and in activating the alkyne and releasing the product enyne.



Scheme 4.

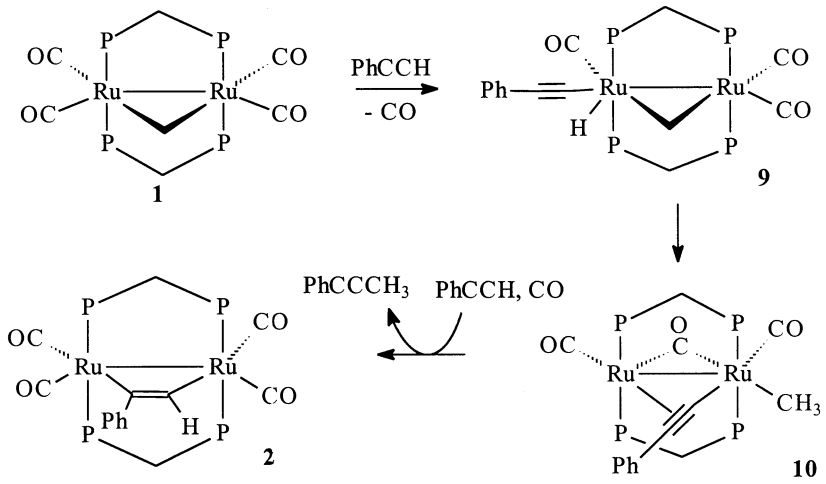
2.3. Oligomerization of phenylacetylene

The reaction of complex **1** with a large excess of PhCCH (1:67) at 75 °C in toluene-d_8 was monitored by ^1H and ^{31}P NMR spectroscopy. The catalysis to give PhCCC(Ph)=CH_2 occurred as described previously, and complex **1** was slowly converted to **2** over 2 days. However, further slow reactions occurred over a period of 10 days, with conversion of complex **2** to an uncharacterized mixture of ruthenium products and with disappearance of essentially all PhCCH and PhCCC(Ph)=CH_2. By precipitation from this solution, a yellow powder was isolated whose ^1H NMR spectrum was similar to the reported spectrum of atactic poly(phenylacetylene) [10]. However, GPC analysis indicated that this yellow powder contained a mixture of oligomeric products with an octamer and a hexamer as the main components. In agreement, the MS analysis of the sample showed major peaks at $m/z = 816$ (octamer) and 612 (hexamer), with less intense peaks at $m/z = 714$ (heptamer) and 510 (pentamer). Given that most PhCCH was consumed before these products were formed, it is likely that, for example, the octamer is really a tetramer of the dimer PhCCC(Ph)=CH_2, but the mechanism of this subsequent oligomerization is obscure.

2.4. The reaction of complex *1* with other alkynes

Complex **1**, as a solution in toluene at 75 °C, reacted slowly with excess 1-hexyne to give a mixture of dimerization products *E*-RC≡C–CH=CHR and RC≡C–C(R)=CH_2 (R = butyl) in a ratio of about 2:1. These products, formed by head-to-head and head-to-tail dimerization respectively, were identified by their known NMR spectra [11] and confirmed by GC–MS. A slow transformation of complex **1** to unidentified ruthenium complexes was also observed during this process. This catalytic reaction is both slower and less selective than the corresponding reaction with PhCCH described above.

The reaction of complex **1** in CD_2Cl_2 at 20 °C led to slow precipitation of a fine purple solid and the corresponding reaction in toluene-d_8 at 75 °C gave a similar product more rapidly. This material was largely insoluble in common organic solvents, and was tentatively identified as polyacetylene. Complex **1** remained essentially unreacted during this process. Complex **1** failed to react with the alkynes PhCCMe, PhCCPh or 3-hexyne at 75 °C in toluene.



Scheme 5.

3. Conclusions

The diruthenium μ-methylenc complex [Ru_2(μ-CH_2)(CO)$_4$(μ-dppm)$_2$] (**1**) displayed unusual catalytic activity toward the dimerization and oligomerization of the terminal alkyne PhCCH. In toluene solution at 75 °C, complex **1** is a catalyst for the selective dimerization of PhC≡CH to give PhCCC(Ph)=CH_2 and appears to be the first complex to display such selectivity.

4. Experimental

All manipulations were carried out under a dry nitrogen atmosphere using either standard Schlenk techniques or a glove box. Toluene was dried and distilled immediately before use. [Ru_2(μ-CH_2)(CO)$_4$(μ-dppm)2] was synthesized by the reaction of [Ru_2(μ-CO)(CO)$_4$(μ-dppm)$_2$] with CH_2N_2 [9]. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Varian Inova 600 or 400 spectrometer. Mass spectra were recorded using a Finnigan Mat 8200 spectrometer. IR spectra were recorded by using a Perkin–Elmer PE2000 FT IR.

4.1. The dimerization of alkynes in the presence of complex *1*

4.1.1. General procedure

To a solution of **1** (15 mg, 0.0135 mmol) in toluene-d$_8$ (0.5 ml) in an NMR tube was added a known amount of the alkyne. The course of the reaction was then monitored at room temperature or at 75 °C by NMR. The extent conversion of the alkyne to the dimeric product(s) was determined by integration of the respective ^{1}H resonances.

4.1.2. Specific example

To a solution of **1** in toluene-d$_8$ (15 mg, 0.0135 mmol) in a NMR tube was added PhCCH (12 μl, 0.108 mmol), The solution was kept at 75 °C and monitored with time by NMR. After 24 h, no signal resonances for PhCCH could be detected and 2,4-diphenylbut-1-en-3-yne was found to be the only organic product by^{1}H NMR and GC–MS.

NMR data in toluene-d$_8$: 2,4-diphenylbut-1-en-3-yne [11]: $\delta(^1H) = 5.7$ [d, $J = 1$ Hz, HC(H)=C]; 5.9 [d, $J = 1$ Hz, HC(H)–C–]; GC–MS: $m/z = 204$ (M^+). n-BuCC–C(n-Bu)C=CH_2 [11]: $\delta(^1H) = 5.3$ [d, $J = 6$ Hz, –C=CH_AH_B]; 5.1 [d, $J = 6$ Hz, –C=CH_AH_B]; GC–MS: $m/z = 164$ (M^+), E-n-BuCCCH=CH-n-Bu [11]: $\delta(^1H) =$ 6.04 [dt, $J = 16$, 6 Hz, BuCH=CH–]; 5.1 [d, $J = 16$ Hz, BuCH=CH–]; GC–MS: $m/z = 164$ (M^+).

4.2. ^2H NMR studies of the dimerization of PhC≡CD

To a solution of **1** (15 mg, 0.0135 mmol) in toluene in an NMR tube was added PhCCD (20 μl, 0. 178 mmol). The solution was kept at 75 °C for 24 h and then checked by ^{2}H NMR for the deuterium distribution. NMR in toluene-d$_8$: $\delta(^2H) = 5.6$ and 5.7 [s, PhCC–C(Ph)=CD_2]; 1.6 [s, PhCCH_2D]. GC–MS: $m/z =$ 206(M^+).

5. [Ru_2{μ-η^1:η^1-C(Ph)C(H)}(CO)$_4$(μ-dppm)$_2$] (2)

a) To a solution of **1** in toluene-d$_8$ (15 mg, 0.0135 mmol) in a NMR tube was added PhCCH (30 μl, 0.270 mmol). The solution was kept at 75 °C for 48 h and at this stage, only complex **2** and a small amount of **1** were present as the ruthenium compounds in solution. NMR of **2** in toluene-d$_8$: $\delta(^1H) = 8.2$ [s, 1H, C(Ph)CH]; 4.0 [m, 2H, P–

C*H*–P]; 2.6 [m, 2H, P–CH–P]. $\delta(^{31}P) = 32.5$ [m, dppm]; 34.5 [m, dppm].

b) To a solution of $[Ru_2(\mu\text{-CO})(CO)_4(\mu\text{-dppm})_2]$ (**3**) in toluene-d_8 (20 mg, 0.018 mmol) in an NMR tube was added PhCCH (10 μl, 0.09 mmol). The solution was then kept at 75 °C for 1 h. At this point, the only complex present in solution was **2**. IR (Nujol, cm^{-1}): 1992, 1988, 1980 and 1950 [terminal CO]; 1590 [–C=C–]. The NMR data were as reported above. For a sample prepared by the reaction of PhCCH with ^{13}CO labeled **3**: $\delta(^{13}C) = 218$ [m, terminal CO]; 209 [m, terminal CO]; 208 [m, terminal CO]; 207 [m, tenninal CO]. The product was obtained as a yellow solid by precipitation with ether. *Anal.* Calc. for $C_{62}H_{50}O_4P_4Ru_2$: C, 62.8; H, 4.2. Found: C, 62.3; H, 4.0%.

Acknowledgements

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