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Reaction of acetylenes with edge double-bridged triruthenium complexes

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Abstract - The complex $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$, [1], reacts with aryl acetylenes at 25 °C (Ar = Ph, p-$CH_3C_6H_4$, or p-$(CH_3O)C_6H_4$) giving only dinuclear products $Ru_2\{\mu\text{-}O{=}CNMe_2,\mu\text{-}\sigma,\pi\text{-}C(Ar){=}CH(Ar)\}(CO)_6$, [5a,b,c] in 50–80% yield, and $Ru_2\{\mu\text{-}\eta^2,\eta^4\text{-}C(Ar){=}C(Ar)\text{-}C(Ar){=}C(Ar)\}(CO)_6$, [6a,b,c], in 20–25% yield. Crystal and molecular structures have been determined for [5b] and for $Ru_2\{\mu\text{-}O{=}CNMe_2,\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH(Ph)\}(CO)_5(PPh_3)$, [9], both existing exclusively as the vic isomers in the solid state. At -50 °C, ^1H or ^{13}C NMR spectra of these complexes indicate two isomers in solution (vic and gem) which are rapidly interconverting. Through complexes of $Ph_2{}^{13}C_2$, it is possible to assign the predominant species in solution as the gem isomer in both cases. ▱Reaction of phenylacetylene with [1] gives an unstable product which can be isolated only as the PPh_3 substituted complex $Ru_2\{\mu\text{-}O{=}CNMe_2,\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5(PPh_3)$, [10]. Only the Markownikoff adduct is seen, and no NMR signal averaging occurs between the vic and gem isomers at 23 °C. Crystal and molecular structure reveal exclusively the gem isomer in the solid state. ▱Reaction of [1] with hexafluorobut-2-yne gives the dinuclear adduct, $Ru_2\{\mu\text{-}H,\mu\text{-}O{=}CNMe_2,\mu\text{-}C(CF_3){=}C(CF_3)\}(CO)_6$, [11], in 56% yield, with no evidence of a $\mu\text{-}\sigma,\pi$-isomer. ▱Complex [5b] reacts with propyne at 23 °C to give the all-cis-1-butadienyl complex $Ru_2\{\mu\text{-}O{=}CNMe_2,\mu\text{-}\sigma,\pi\text{-}CMe{=}C(H)R\}(CO)_6$, R= cis-C(p-tol)=CH(p-tol), [12], 48% yield; crystal and molecular structure show the gem isomer in the solid state.

INTRODUCTION

Previously, we reported the reaction of but-2-yne with $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$, [1], which gives the trinuclear η^3-methallyl complex $Ru_3\{\eta^3\text{-}CH_2CH(Me)\}\{\mu\text{-}C(O),\mu\text{-}O{=}C(NMe_2)\}(CO)_8$, [2], as principal product along with small amounts of two dinuclear complexes $Ru_2\{\mu\text{-}O{=}CNMe_2,\mu\text{-}\sigma,\pi\text{-}C(Me){=}CH(Me)\}(CO)_6$, [3], and $Ru_2\{\mu\text{-}O{=}CNMe_2,\mu\text{-}O{=}C\text{-}CMe{=}CMe\text{-}(\eta^2\text{-}CMe{=}CH(Me)\}(CO)_5$, [4] (ref. 1). By contrast, we found that aryl acetylenes or hexafluoro-2-butyne give principally dinuclear products whose elucidation through ^{13}C-enriched materials and further structural and synthetic studies are presented here.

STUDIES OF THE μ-σ,π-VINYL COMPLEXES OF DIARYL ACETYLENES

There is a problem in assigning solution structures of the $\mu\text{-}\sigma,\pi$-vinyl complexes, as illustrated in Fig. 1. The presence of principal resonances accompanied by a closely matching set of smaller peaks indicates two isomers in solution in unequal population. For example, two doublets are identified, each as the ^2C resonance of the $\mu\text{-}\sigma,\pi$-vinyl group in the two isomers. The two sets of signals merge at +30 °C (ref. 1) indicating rapid equilibration in solution.

Assignment of the sets of resonances to the two isomers was not possible, nor was it possible to identify the ^1C resonance of the $\mu\text{-}\sigma,\pi$-vinyl group. For example, eight maxima are observed in the carbonyl region (δ = 210 to 185 ppm), thus the resonance of ^1C must be located there. However, none of the ^1H-coupled resonances (see insert in Fig. 1) shows doubling, due to the fact that the coupling constant $J^2(^1H\text{-}C\text{-}^{13}C)$ must be close to zero (ref. 2). We thus prepared a ^{13}C-enriched acetylene and its diruthenium complexes according to the equations shown in Scheme 1 (ref. 3).

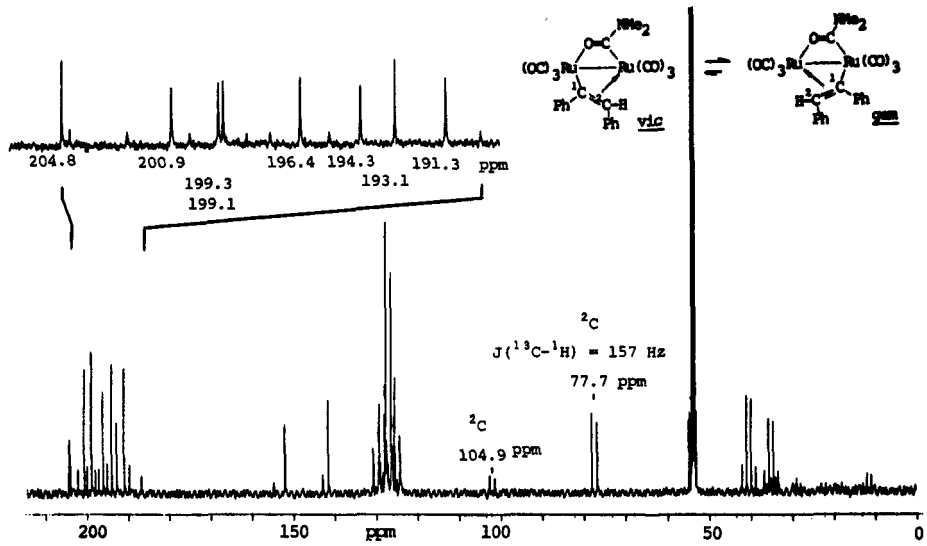
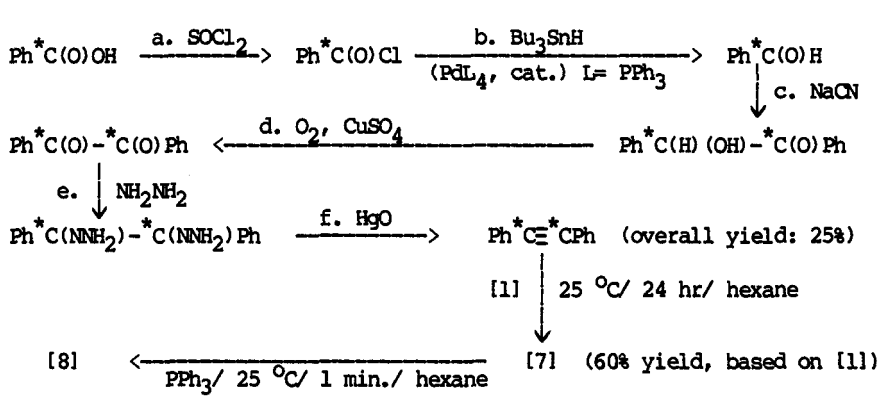


Fig. 1. $^{13}C(^1H$ coupled) NMR, 125.8 MHz, CD_2Cl_2 sol'n for [5a] at -50 °C.

The ^{13}C NMR spectra of $Ru_2\{\mu$-O=CNMe$_2$,μ-σ,π-$^*C(Ph)=^*CH(Ph)\}(CO)_6$, [7], and $Ru_2\{\mu$-O=CNMe$_2$, μ-σ,π-$^*C(Ph)=^*CH(Ph)\}(CO)_5(PPh_3)$, [8], $^*C$= ^{13}C, are shown in Fig. 2. The ^1C resonances are easily identified in each of the two spectra as the strong doublets arising from ^{13}C-^{13}C coupling in the doubly labelled σ,π-vinyl group. Each strong doublet represents the ^1C resonance of the major isomer in solution and is accompanied by a corresponding resonance of lower intensity due to the minor isomer. In the upper scan of Fig. 2, both the principal and the accompanying ^1C resonances are doublets. In the lower scan, however, the ^1C resonance of the major isomer is a doublet but that of the minor isomer is a doublet of doublets. This must arise from ^{31}P coupling, and would be expected to be greater in the vic isomer (10 Hz) than in the gem isomer (not resolvable).

From the above analysis, we assign the gem isomer as predominant in solution for [8], which is presumably also the case for [7]. Due to the similarity in the ^{13}C NMR spectra of the diphenyl and di(p-tolyl) acetylene derivatives, [5a] and [5b], we assume similar distribution of isomers in their solutions. Thus, predominance of the gem isomer is indicated in solution while the single crystal obtained for [5b] is exclusively the vic isomer (ref.1).

Scheme 1 Synthesis of $Ru_3\{\mu$-O=CNMe$_2$,μ-σ,π-$^*C(Ph)=^*CH(Ph)\}(CO)_5L$
L= CO, [7]; L= PPh_3, [8].



*C = ^{13}C

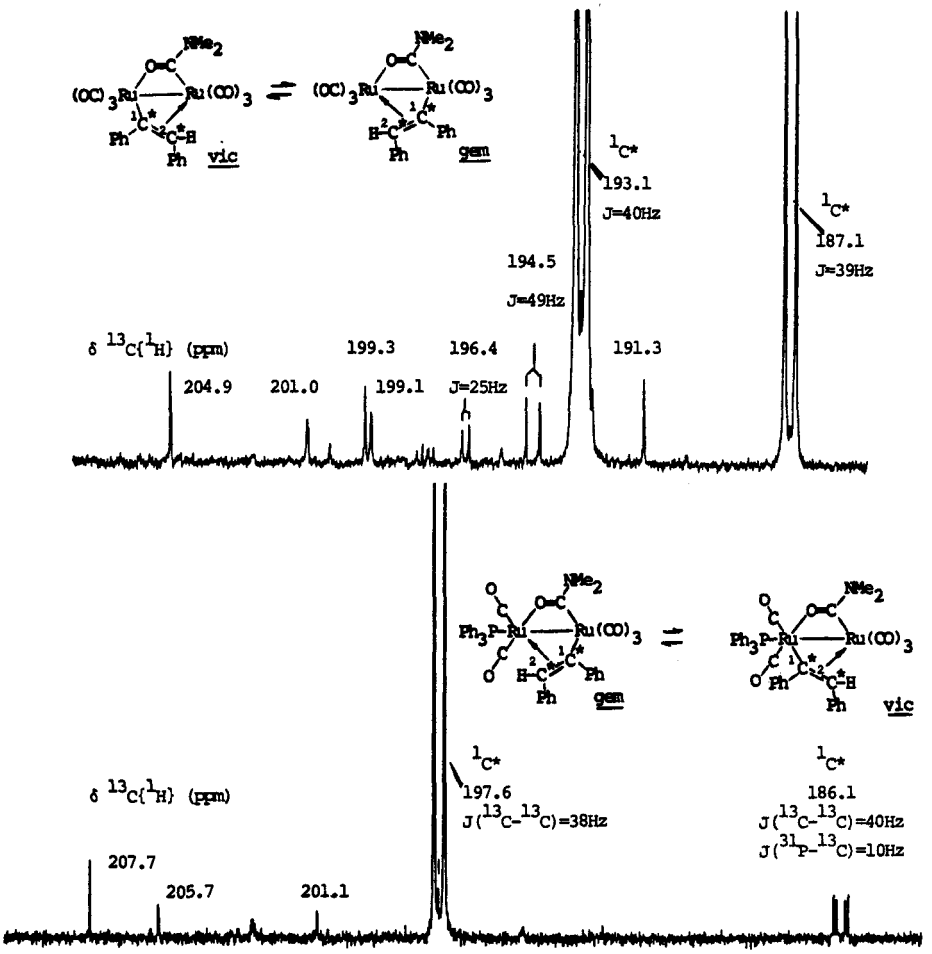


Fig. 2. $^{13}C\{^1H\}$ NMR spectra, 125.8 MHz, in CD_2Cl_2, -50 °C, carbonyl region, for $Ru_2\{\mu$-O=CNMe$_2$,μ-σ,π-*C(Ph)=*CH(Ph)$\}$(CO)$_5$L. Upper trace: L= CO, [7]. Lower trace: L= PPh_3, [8].

In order to ascertain the predominant isomer in the solid state for a substituted derivative, a structure was determined for $Ru_2\{\mu$-O=CNMe$_2$,μ-σ,π-C(p-tol)=CH(p-tol)$\}$(CO)$_5$(PPh_3), [9], see Fig. 3; only the vic isomer appears in the solid state, as in the unsubstituted derivative [5b] (ref. 1).

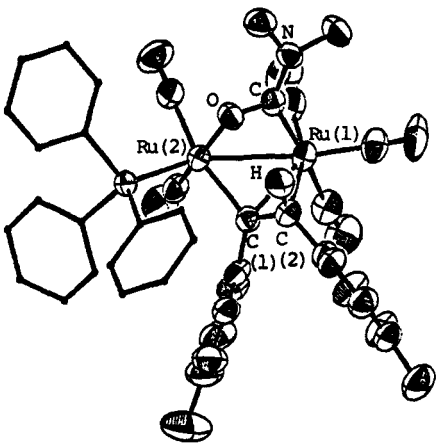


Fig. 3. ORTEP of [9].

	d/Å
Ru(1)-Ru(2)	= 2.746(1)
Ru(1)-C(2)	= 2.329(6)
Ru(1)-C(1)	= 2.327(6)
Ru(2)-C(1)	= 2.085(6)
C(1)-C(2)	= 1.416(9)
O -C	= 1.282(7)

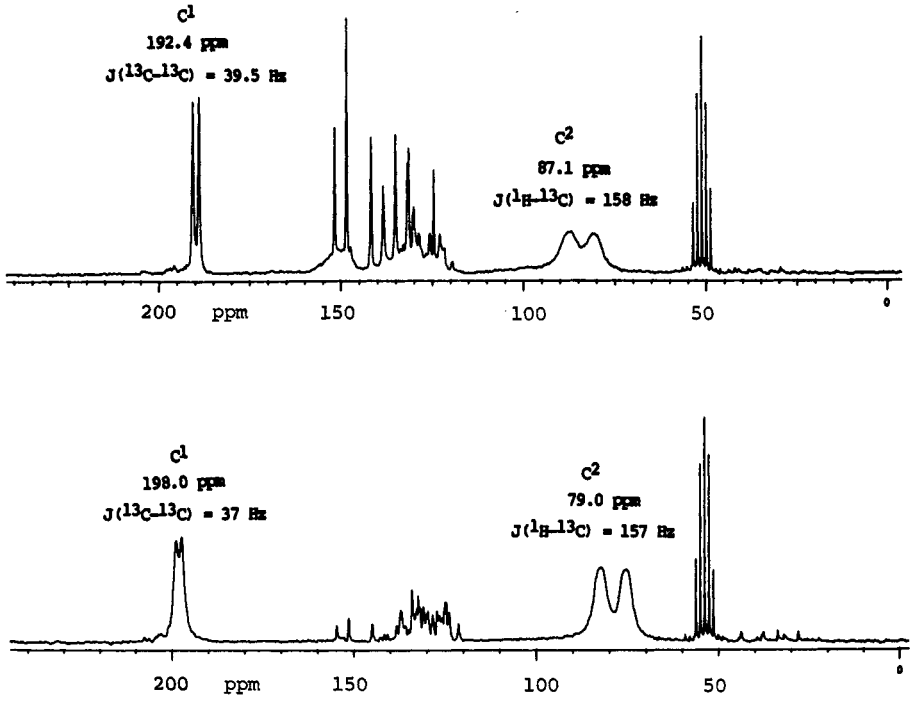


Fig. 4. $^{13}C(^{1}H$-coupled) NMR spectra at 22.5 MHz, in CD_2Cl_2, +23 °C, showing population-weighted chemical shift-averaged resonances for the ^{1}C and ^{2}C σ,π-vinyl group resonances (among other peaks) for $Ru_2\{\mu$-O=CNMe$_2$,μ-σ,π-$^{*}C(Ph)=^{*}CH(Ph)\}(CO)_5L$. Upper trace: L= CO, [7]. Lower trace: L= PPh_3, [8].

At room temperature, the separate ^{13}C NMR signals of the gem and vic isomers are seen to merge giving signals shown in part in Fig. 4 above. The averaged ^{1}C resonances do not show any coupling to ^{1}H; the splitting observed in these peaks is the ^{13}C–^{13}C coupling with a small ^{31}P–$^{13}C(1)$ of ca 3 Hz in complex [8] (lower trace), observed in the limiting spectrum at -50 °C .

The resonances for the ^{2}C atoms have not completely coalesced at 23 °C, the highest we could reach without thermal decomposition. In both the upper and lower traces of Fig. 4 these still broadened resonances show a peak-to-peak separation close to the ^{1}H–^{13}C coupling observed in the limiting spectra (see Fig. 1). Preservation of the full ^{1}H–^{13}C coupling in the averaged ^{2}C signals indicates a tautomerization pathway involving the intact vinyl group, see path A in Fig. 5. Motion of hydrogen in the equilibration (Path B) can be excluded since it would have required a smaller peak-to-peak separation arising from an average between J (^{1}H–$^{13}C(1)$) = ca. 0 Hz and J (^{1}H–$^{13}C(2)$) = 157 Hz.

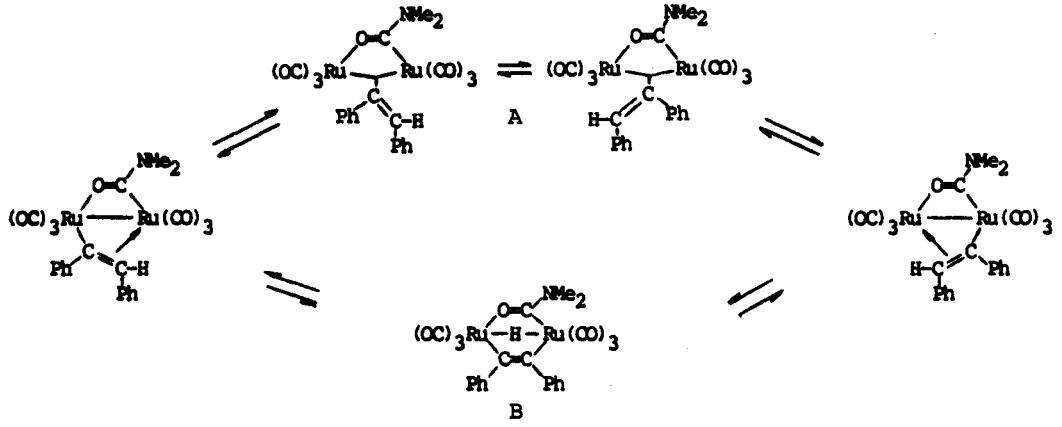
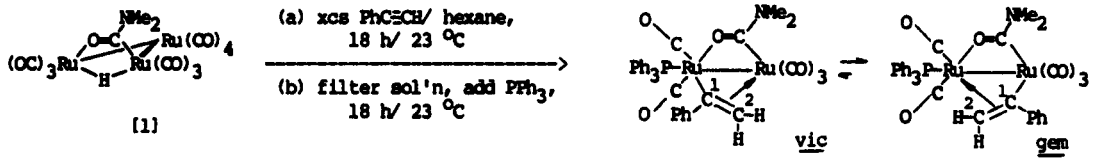


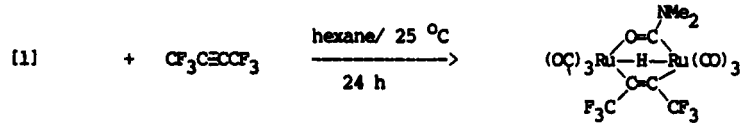
Fig. 5. Possible pathways for σ,π-vinyl group tautomerism.

STUDIES WITH OTHER ACETYLENES

Scheme 2 Synthesis of Phenylacetylene and Hexafluorobut-2-yne Complexes



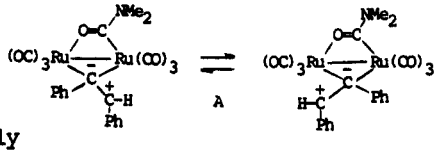
[10] (yield 75% based on [1])



[11] (yield: 56% based on [1])

The reaction of phenylacetylene with [1] gives an unstable product which can be isolated only as the PPh_3 substituted complex [10], Scheme 2. NMR spectra again indicate the presence of two isomers, vic and gem, but only of the Markownikoff adduct as shown in Scheme 2: the ^2C resonances in the ^1H-coupled-^{13}C NMR spectrum of [10] appear as triplets, δ= 92.88 and 59.24 ppm, $J(^1H-^{13}C(2))$ = 159 Hz, respectively.

No merging of the signals of the vic and gem isomers of [10] is observed at 23 °C, denoting a much slower tautomerism as compared to complexes of diphenyl or di(p-tolyl) acetylenes. There is no phenyl group substituent on ^2C of the σ,π-vinyl group in [10]; this suggests a phenyl group stabilized charge-transfer intermediate or transition state may be traversed for the intact vinyl group tautomerism, Path A of Fig. 5. Charge-transfer structures for the tautomerism are supported by molecular orbital studies of methylene-bridged transition metal complexes (ref. 4). The M_2C ring system may accommodate six electrons, thus favoring a polar structure for the vinyl-dimetallocyclopropane.



Crystal and molecular structure of [10] reveal exclusively the gem isomer in the solid, see Fig. 6.

The reaction of [1] with hexafluorobut-2-yne (ref. 5) is shown in Scheme 2. The product, [11], contains an ^1H resonance at -14.60 ppm indicating the presence of hydrogen bridging between the metal atoms. We thus assign a structure as shown in Scheme 2; there is no evidence for any σ,π-vinyl adduct. ^{13}C NMR of [11] (ref. 5) shows two distinct resonances for each of the two types of carbon atoms in the μ-C(CF$_3$)=C'(C'F$_3$) group. NMR studies from -60 to +90 °C show no equilibration of the signals; thus complex [11] does not participate in any rapid tautomerism in this temperature range. This structure type was also excluded from rapid tautomerism for the diphenyl and di(p-tolyl) derivatives, see Fig. 5.

The reaction of [5b] with $CH_3C{\equiv}CH$ was examined, see Scheme 3 (ref. 6). An all cis butadiene telomerization product is obtained which crystallizes as the gem-{μ-O=CNMe$_2$,μ-σ,π-vinyl} isomer, Fig. 7. This product may represent the intermediate leading to the type of complexes [4] and [6] isolated in the reaction of [1] with other acetylenes (ref. 1).

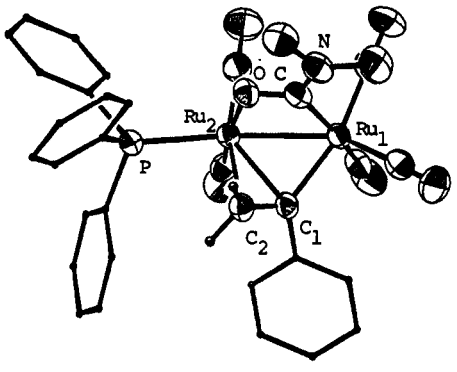
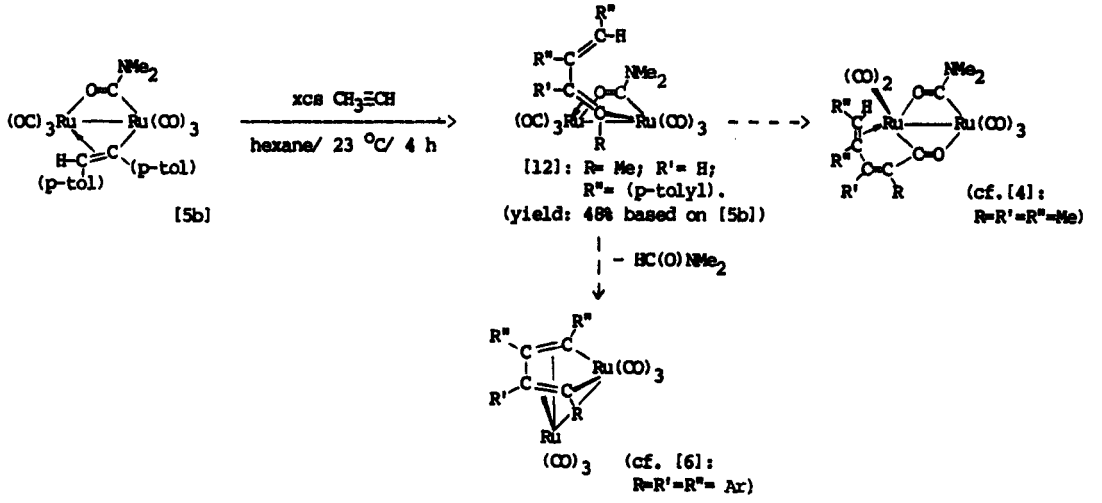


Fig. 6. ORTEP of [10].

	d/Å
Ru(1)-Ru(2)	= 2.720(1)
Ru(1)-C(1)	= 2.130(6)
Ru(2)-C(1)	= 2.319(5)
Ru(2)-C(2)	= 2.331(6)
C(1)-C(2)	= 1.396(8)

Scheme 3 Synthesis of Complex [12] and Its Proposed Relationship to Complexes [4] and [6].



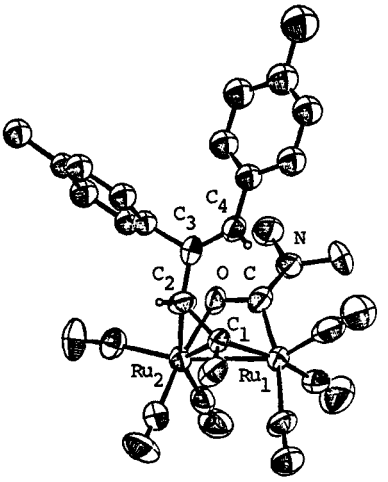


Fig. 7. ORTEP of [12].

	d/Å
Ru(1)-Ru(2)	= 2.725 (2)
Ru(1)-C(1)	= 2.107(15)
Ru(2)-C(1)	= 2.257(17)
Ru(2)-C(2)	= 2.327(19)
C(1)-C(2)	= 1.442(20)
C(2)-C(3)	= 1.493(22)
C(3)-C(4)	= 1.306(20)

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