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# REACTIONS OF TRANSITION METAL ACETYLIDES

## VI *. SOME ADDITION REACTIONS OF SUBSTITUTED STYRENES WITH $Ru(C_2R)(L)_2(\eta\text{-}C_5H_5)$ (R = Me OR Ph; $L_2$ = (CO, $PPh_3$), $(PPh_3)_2$ OR (dppe)). X-RAY CRYSTAL STRUCTURE OF $Ru\{C[=C(CN)_2]CPh{=}CH(C_6H_4NO_2\text{-}4)\}(dppe)(\eta\text{-}C_5H_5)\cdot 0.5CH_2Cl_2$

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### Summary

Further studies of the reactions between ruthenium σ-acetylide complexes and electrophilic olefins CHAr=C(CN)(X) (Ar = $C_6H_4NO_2$-4, Ph; X = CN; Ar = $C_6H_4NO_2$-4, X = $CO_2Et$) have shown the formation of allylic, butadienyl, and in one case, cyclobutenyl complexes. The direction of addition is such that the =C(CN)(X) group becomes attached to the α-carbon of the acetylide. This is confirmed by the X-ray structure of $Ru\{C[=C(CN)_2]CPh{=}CH(C_6H_4NO_2\text{-}4)\}(dppe)(\eta\text{-}C_5H_5)\cdot 0.5CH_2Cl_2$, crystals of which are monoclinic, space group $C2/c$ with cell dimensions $a$ 28.81(1), $b$ 9.661(2), $c$ 30.782(8) Å, $\beta$ 95.02 (3)°, and $Z = 8$. The structure was refined by a least-squares procedure with the use of 4291 statistically significant reflections [$I > 2.5\sigma(I)$] to $R$ 0.075 and $R_w$ 0.076.

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### Introduction

We have recently described the reactions of tetracyanoethylene ($C_2(CN)_4$, tcne) with several ruthenium acetylide complexes of the type $Ru(C_2R)(L)_2(\eta\text{-}C_5H_5)$ (R = Me, Ph; $L_2 = (PPh_3)_2$, (CO, $PPh_3$), (dppe), etc.) which result in a [2 + 2]-cycloaddition of the cyano-olefin to the acetylide moiety [2]. The resulting σ-cyclobutenyl complexes **1** undergo a facile ring-opening to form the corresponding σ-2-butadienyl derivatives **2**, which in some instances react further, replacing a ligand L with the double-bond of the butadiene which is furthest from the metal.

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* For part V see ref. 1.

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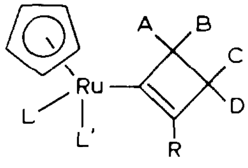
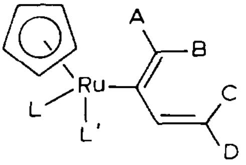
The complexes so formed (**3**) can be considered to contain an $\eta^3$-allylic ligand, which also has properties similar in some respects to those expected for a methylenemetallacyclobutene. The butadienyl complex is formally the result of inserting the metal-bonded C≡C unit between the two olefinic carbons of the cyanocarbon. We were interested to determine what factors influenced these unusual reactions of the acetylide complexes and have therefore examined the effect of changing the substituents on the olefinic carbons. This paper describes some of these studies with substituted styrenes.



(1)



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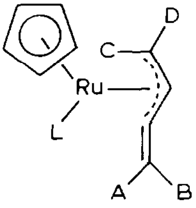


(3)

| | L | L' | R | A | B | C | D |
|---|---|---|---|---|---|---|---|
| 3a | $PPh_3$ | | Ph | CN | CN | H | $C_6H_4NO_2$-4 |
| 3b | $PPh_3$ | | Me | CN | CN | H | $C_6H_4NO_2$-4 |
| 2c | CO | $PPh_3$ | Ph | CN | CN | H | $C_6H_4NO_2$-4 |
| 2d | dppe | | Ph | CN | CN | H | $C_6H_4NO_2$-4 |
| 3e | $PPh_3$ | | Ph | CN | CN | H | Ph |
| 1f | CO | $PPh_3$ | Ph | CN | CN | H | Ph |
| 3g | $PPh_3$ | | Me | CN | $CO_2Et$ | H | $C_6H_4NO_2$-4 |
| 2h | CO | $PPh_3$ | Ph | CN | $CO_2Et$ | H | $C_6H_4NO_2$-4 |

The lack of reaction observed with simple olefins such as ethylene or acrylonitrile prompted us to examine first some α, α-dicyanostyrenes containing different groups on the phenyl ring, $4\text{-}RC_6H_4CH{=}C(CN)_2$ ($R = NO_2$, H, $NMe_2$). These compounds are readily prepared by condensation of malonitrile with the corresponding benzaldehyde (Knoevenagel reaction).

## Results and discussion

The reactions between $4\text{-}NO_2C_6H_4CH{=}C(CN)_2$ and $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ (R = Ph or Me) were carried out in refluxing toluene and gave in each case a complex analysing for a 1 : 1 adduct less one $PPh_3$ ligand. These complexes (**3a** and **3b**) were obtained as yellow-orange solids in 78 and 84% yields, respectively, which contained one or half a mole of solvated $CH_2Cl_2$. In the IR spectra, $\nu$(CN) bands are found between 2200–2220 $cm^{-1}$ and $\nu$(C=C) at ca. 1590 $cm^{-1}$. The retention of the nitro group is confirmed by the observation of $\nu$(NO) bands at ca. 1260 $cm^{-1}$. The $^1H$ NMR spectra contained the expected resonances at $\delta$ ca. 4.6 ($C_5H_5$), 3.0 (=CH) and 2.2 (Me, for **3b** only), in addition to the resonances of the aromatic protons. The mass spectrum of **3a** contained a molecular ion at $m/z$ 729; for **3b**, the highest mass ion was at $m/z$ 405, corresponding to $[M - PPh_3]^+$. The compounds are formulated as two more examples of the allylic complexes, but the spectroscopic

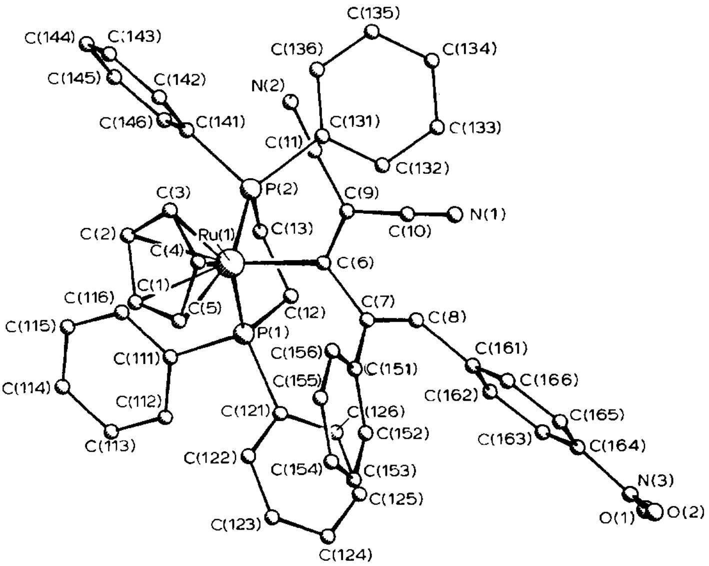


Fig. 1. PLUTO plot of Ru{C[=C(CN)$_2$]CPh=CH(C$_6$H$_4$NO$_2$-4)}(dppe)($\eta$-C$_5$H$_5$) (**2d**).

evidence is not sufficient to assign the geometry of the allylic group unambiguously, in other words, to enable the direction of addition to be determined.

An adduct (**2c**) was obtained in 74% yield from the nitrophenyl olefin and Ru(C$_2$Ph)(CO)(PPh$_3$)($\eta$-C$_5$H$_5$). The IR spectrum showed a single $\nu$(CO) band at 1962 cm$^{-1}$ and $\nu$(CN) at 2240 and 2216 cm$^{-1}$, while the $^1$H NMR spectrum contained the expected resonances at $\delta$ 5.26 (=CH) and 4.74 (C$_5$H$_5$) in addition to the aromatic resonances. In this case, the $^1$H NMR spectrum also contained a resonance at $\delta$ 4.81, which had disappeared after 30 min. This signal is assigned to

TABLE 1

BOND DISTANCES (Å) FOR Ru{C[=C(CN)$_2$]CPh=CHC$_6$H$_4$NO$_2$-4}(dppe)($\eta$-C$_5$H$_5$) (**2d**)

| | | | |
|---|---|---|---|
| P(1)–Ru(1) | 2.283(2) | P(2)–Ru(1) | 2.319(3) |
| C(1)–Ru(1) | 2.198(10) | C(2)–Ru(1) | 2.240(9) |
| C(3)–Ru(1) | 2.243(10) | C(4)–Ru(1) | 2.250(10) |
| C(5)–Ru(1) | 2.235(12) | C(6)–Ru(1) | 2.063(8) |
| C(12)–P(1) | 1.831(11) | C(111)–P(1) | 1.871(5) |
| C(121)–P(1) | 1.839(7) | C(13)–P(2) | 1.860(9) |
| C(131)–P(2) | 1.846(7) | C(141)–P(2) | 1.844(8) |
| C(13)–C(12) | 1.513(14) | C(2)–C(1) | 1.421(15) |
| C(5)–C(1) | 1.426(15) | C(3)–C(2) | 1.456(14) |
| C(4)–C(3) | 1.392(16) | C(5)–C(4) | 1.419(15) |
| C(7)–C(6) | 1.517(12) | C(9)–C(6) | 1.374(13) |
| C(8)–C(7) | 1.326(14) | C(151)–C(7) | 1.469(12) |
| C(161)–C(8) | 1.516(11) | C(10)–C(9) | 1.468(14) |
| C(11)–C(9) | 1.452(15) | N(1)–C(10) | 1.132(14) |
| N(2)–C(11) | 1.141(15) | O(1)–N(3) | 1.208(16) |
| O(2)–N(3) | 1.226(16) | C(164)–N(3) | 1.483(13) |
| C(0)–Cl(0) | 1.757(28) | | |

TABLE 2

ATOMIC COORDINATES (Ru$\times10^5$; other atoms$\times10^4$) FOR NON-HYDROGEN ATOMS IN Ru{C[=C(CN)$_2$]CPh=CHC$_6$H$_4$NO$_2$-4}(dppe)($\eta$-C$_5$H$_5$) (**2d**)

| Atoms | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Ru(1) | 31718(2) | 15599(7) | 10279(3) |
| P(1) | 3157(1) | 3923(2) | 1023(1) |
| P(2) | 3009(1) | 1846(2) | 1747(1) |
| C(12) | 3245(3) | 4581(9) | 1581(4) |
| C(13) | 2934(4) | 3727(9) | 1849(4) |
| C(1) | 2656(4) | 1412(10) | 459(3) |
| C(2) | 2507(3) | 506(10) | 783(4) |
| C(3) | 2874(3) | −528(10) | 847(4) |
| C(4) | 3206(3) | −216(10) | 559(4) |
| C(5) | 3096(3) | 1015(11) | 320(4) |
| C(6) | 3876(3) | 1303(8) | 1191(3) |
| C(7) | 4260(3) | 2183(9) | 1026(4) |
| C(8) | 4483(3) | 2993(10) | 1322(4) |
| C(9) | 4046(3) | 117(10) | 1393(4) |
| C(10) | 4544(4) | −229(11) | 1439(4) |
| C(11) | 3761(4) | −949(11) | 1570(4) |
| N(1) | 4927(3) | −509(12) | 1475(4) |
| N(2) | 3553(3) | −1821(9) | 1710(4) |
| N(3) | 6117(4) | 6396(14) | 1185(4) |
| O(1) | 6105(3) | 7529(10) | 1350(4) |
| O(2) | 6429(3) | 5900(12) | 988(4) |
| Cl(0) | 476(3) | 1669(18) | 2563(3) |
| C(0) | 0 | 2809(41) | 25 |
| C(112) | 2558(2) | 6033(6) | 644(2) |
| C(113) | 2127(2) | 6667(6) | 545(2) |
| C(114) | 1720(2) | 6004(6) | 645(2) |
| C(115) | 1744(2) | 4707(6) | 845(2) |
| C(116) | 2175(2) | 4073(6) | 945(2) |
| C(111) | 2582(2) | 4736(6) | 844(2) |
| C(122) | 3479(2) | 4839(6) | 250(2) |
| C(123) | 3745(2) | 5646(6) | −11(2) |
| C(124) | 4063(2) | 6602(6) | 181(2) |
| C(125) | 4115(2) | 6750(6) | 634(2) |
| C(126) | 3850(2) | 5942(6) | 894(2) |
| C(121) | 3532(2) | 4987(6) | 702(2) |
| C(132) | 3841(2) | 1990(7) | 2278(2) |
| C(133) | 4149(2) | 1677(7) | 2639(2) |
| C(134) | 4021(2) | 730(7) | 2949(2) |
| C(135) | 3585(2) | 94(7) | 2898(2) |
| C(136) | 3277(2) | 407(7) | 2536(2) |
| C(131) | 3404(2) | 1354(7) | 2226(2) |
| C(142) | 2360(2) | −297(7) | 1790(3) |
| C(143) | 1939(2) | −882(7) | 1888(3) |
| C(144) | 1619(2) | −93(7) | 2096(3) |
| C(145) | 1720(2) | 1281(7) | 2207(3) |
| C(146) | 2141(2) | 1866(7) | 2109(3) |
| C(141) | 2461(2) | 1077(7) | 1901(3) |
| C(152) | 4491(2) | 3206(5) | 338(2) |
| C(153) | 4593(2) | 3074(5) | −95(2) |
| C(154) | 4568(2) | 1780(5) | −297(2) |
| C(155) | 4440(2) | 618(5) | −65(2) |
| C(156) | 4339(2) | 750(5) | 367(2) |

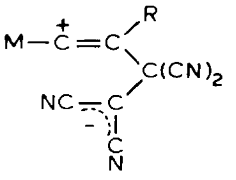
TABLE 2 (continued)

| | | | |
|---|---|---|---|
| C(151) | 4364(2) | 2044(5) | 569(2) |
| C(162) | 4922(2) | 5224(6) | 1424(2) |
| C(163) | 5320(2) | 6033(6) | 1400(2) |
| C(164) | 5712(2) | 5474(6) | 1231(2) |
| C(165) | 5707(2) | 4105(6) | 1087(2) |
| C(166) | 5309(2) | 3296(6) | 1111(2) |
| C(161) | 4917(2) | 3855(6) | 1280(2) |

the ($C_5H_5$) resonance of the cyclobutenyl precursor (**1c**) which rapidly isomerises to the butadienyl complex. A similar complex (**2d**) was obtained from $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ in 88% yield. In both cases, the analytical and spectral data are consistent with either of the isomeric cyclobutenyl or butadienyl formulations, and to determine which was correct, and also the direction of addition, an X-ray structural study of complex **2d** was carried out. Interestingly, both the microanalysis and the $^1H$ NMR spectrum confirm the presence of a mole of EtOH per mole of **2d**. This is evidently the same as present in the precursor acetylide complex, and its removal from solution suggests a remarkable degree of selective incorporation of this molecule into the crystal lattice of **2d**. However, the crystal structure determination was carried out on a sample which was recrystallised from $CH_2Cl_2$, and the crystal was found to be a 2/1 solvate.

The molecular structure of **2d** is shown in Fig. 1. Selected bond lengths are collected in Table 1 and atomic coordinates in Table 2. The complex is the σ-butadienyl derivative, the dicyanomethylene group being attached to the carbon bearing the metal, that is, the sterically least hindered carbon. The ruthenium atom is nearly octahedrally coordinated by the cyclopentadienyl group [Ru–C(cp), 2.23 Å (av.)], two P atoms of the dppe ligand [Ru–P, 2.283(2), 2.319(3) Å], and the C of the butadienyl ligand [Ru–C(6) 2.063(8) Å], as shown by the angles P(1)–Ru–P(2) [83.2(1)°], P(1)–Ru–C(6) [98.0(2)°] and P(2)–Ru–C(6) [93.4(3)°]. As found with the original tcne adduct, the butadienyl group is significantly non-planar [torsion angle C(8)–C(7)–C(6)/C(7)–C(6)–C(9) 82.4°] resulting in localisation of the C–C single [C(6)–C(7) 1.517(12) Å] and C=C double bonds [C(7)–C(8) and C(6)–C(9), 1.326(14) and 1.374(13) Å, respectively]. Other structural features are similar to those found in earlier studies and merit no further comment.

The structure found for **2d** is consistent with the initial addition occurring with the carbon bearing the bulky nitrophenyl group becoming attached to the β-carbon of the phenylacetylide residue. It is also consistent with the formation of a dipolar intermediate such as **4** in which the negative end of the dipole is stabilised by the dicyanomethylene group. This is the pattern of addition which has been observed with all reactions of this type to date, and we conclude that it is this feature which directs the mode of addition.



(**4**)

Significantly lower yields of adducts were obtained from the reactions of $\alpha,\alpha$-dicyanostyrene itself (R = H). Only 14% of the allylic complex $Ru\{\eta^3\text{-}CHPhCPhC{=}C(CN)_2\}(PPh_3)(\eta\text{-}C_5H_5)$ (**3e**) was obtained from the reaction carried out in refluxing toluene as for the examples described using the nitro-substituted compound. In more polar solvents, such as tetrahydrofuran or 1,2-dimethoxyethane, the yield increased to 23%, with up to 45% of the acetylide being recovered. TLC examination of the reaction mixtures after heating 1 or 2 d reflux revealed minor amounts of up to seven other components, but these have not been separated and characterised. The IR spectrum of **3e** contained $\nu(CN)$ bands at 2216 and 2204 $cm^{-1}$, while the $^1H$ NMR spectrum contained peaks at $\delta$ 4.61 ($C_5H_5$) and 3.16 (=CH), together with a multiplet for the phenyl protons. We assume that the structure is derived from addition of the styrene in a similar manner to that found for **3e**, so that the complex has the structure illustrated.

With $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$, a 1 : 1 adduct was formed in 81% yield. Analytical data indicate that the product has either the cyclobutenyl or butadienyl formulation; the presence of a $\nu(CO)$ band at 1955 $cm^{-1}$ also confirms that the allylic complex has not been formed. The IR spectrum differs from those of other complexes described above in the absence of any medium to strong intensity bands between 1500–1600 $cm^{-1}$. This feature has also been found for other cyclobutenyl complexes, and on this basis, we tentatively assign to this complex the cyclobutenyl structure **1f**.

No observable reaction occurred between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ and $4\text{-}Me_2NC_6H_4CH{=}C(CN)_2$ under any solvent and temperature conditions analogous to those used in the reactions described above. These results show that the reaction proceeds more readily with increasing electron deficiency of the olefin: the presence of a dicyanomethylene group, as in $CH_2{=}C(CN)_2$, is not sufficient to activate the olefin towards the initial cycloaddition reaction. Further studies are in progress to determine other factors, including the nature of other metal-bonded ligands, which might activate the acetylide to reaction with less electrophilic olefins.

We have also examined the reactions of $4\text{-}NO_2C_6H_4CH{=}C(CN)(CO_2Et)$ with some ruthenium acetylides. With $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, a mixture of at least nine products was obtained, and none were characterised; interestingly, however, and in contrast with the reactions of the dicyano olefin, a considerable amount of the ruthenium acetylide complex was recovered. The methylacetylide complex reacted in toluene to form orange crystals in 62% yield, which give satisfactory analyses for the allylic formulation **3g**. The IR spectrum contains $\nu(CN)$ at 2216 $cm^{-1}$, and ester $\nu(CO)$ bands between 1600–1730 $cm^{-1}$. The $^1H$ NMR spectrum contains the characteristic resonance at $\delta$ 4.6 ($C_5H_5$) and 2.9 (=CH), together with multiplets in the aromatic region of relative intensity 19H. With the carbonyl-triphenylphosphine complex, a 1 : 1 adduct (**2h**) was isolated as bright yellow crystals in 40% yield. The IR spectrum contained $\nu(CN)$ at 2200 and $\nu(CO)$ at 1955 $cm^{-1}$; the ester $\nu(CO)$ bands were found between 1695–1728 $cm^{-1}$. The $^1H$ NMR spectrum contained resonances according with the proposed formula.

We have endeavoured to find satisfactory spectral criteria for distinguishing between the cyclobutenyl (**1**) and butadienyl (**2**) structures, but the lack of suitably stable cyclobutenyl complexes has precluded an unambiguous answer to this problem. One problem has been the tendency of the cyclobutenyl complexes to isomerise rapidly in solution while accumulation of NMR signals occurred; this made it well-nigh impossible to determine the chemical shifts of the carbons of the $C_4$ units in complexes of type **1**. The use of low temperatures was precluded by the tendency for solutions of sufficient concentration to allow recording of the CN resonance to crystallise as the temperature was lowered.

In earlier papers [2], we suggested that the multiplicity of $\nu$(CN) bands in the IR spectrum might provide some indication. Although an empirical relation between the number and intensity of $\nu$(CN) bands and structure appeared to exist for the tcne adducts, such a relationship cannot be used for the complexes obtained in the present study. At present, the best correlation appears to be with the number of medium to strong intensity bands in the region 1500–1600 $cm^{-1}$. All of the complexes we have prepared to date exhibit the following patterns: cyclobutenyl (type **1**), no m or s bands in this region; butadienyl (type **2**), one m to s band at ca. 1510–1520 $cm^{-1}$; allylic (type **3**), one m to s band at ca. 1590–1620 $cm^{-1}$ with in most cases a similar band between 1510–1520 $cm^{-1}$.

In conclusion, the present study has confirmed the tendency for formation of allylic complexes **3** from precursors of the type $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$, where the steric interaction with the secondary bulky $PPh_3$ group may be relieved by its ready dissociation. The butadienyl complexes **2** are formed in less sterically-demanding situations, while in one case, a cyclobutenyl complex **1** was isolated. The possible effects of replacing CN by $CO_2R$ on the olefin on the stability of complexes of type **1** are currently being explored.

## Experimental

The following instruments were used to obtain spectra: Perkin–Elmer 683 double beam (IR; as Nujol mulls between NaCl plates, calibrated with the 1601 $cm^{-1}$ band of a polystyrene film); Varian T60 ($^1H$ NMR at 60 MHz), Bruker WP80 ($^1H$ NMR at 80 MHz, $^{13}C$ NMR at 20.1 MHz); AEI-GEC MS 3074 double beam (mass spectra, at 70 eV ionising energy, 8 kV accelerating potential). Microanalyses were by the Canadian Microanalytical Service, Vancouver.

All reactions were carried out in a nitrogen atmosphere, but no special precautions were used to exclude oxygen during work-up. Chromatography was carried out on columns of alumina (Brockmann Type 507C, neutral, from Fluka) initially packed in light petroleum, or on thin-layer plates (20 × 20 cm, coated with Merck Kieselgel $GF_{254}$, Type 60). All solvents were dried and redistilled before use. Literature methods were used to prepare $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ (R = Me [3], Ph [4]), $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ [3], $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ [3], and the olefins $C(CN)_2{=}CH(C_6H_4X\text{-}4)$ (X = $NO_2$, H, $NMe_2$) and $C(CN)(CO_2Et){=}CH(C_6H_4NO_2\text{-}4)$ [5].

### *Reactions of* $C(CN)_2{=}CH(C_6H_4NO_2\text{-}4)$

*(a) With* $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. The olefin (213 mg, 0.89 mmol) was added to a stirred solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (715 mg, 0.90 mmol) in toluene (40 ml). After heating at reflux point for 6 h, a dark red solution has formed. Evaporation to dryness and chromatography (alumina) afforded an orange band, eluted with $CH_2Cl_2$. Recrystallisation ($CH_2Cl_2$/light petroleum) gave orange crystals of $Ru[\eta^3\text{-}CH(C_6H_4NO_2)CPhC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)\cdot CH_2Cl_2$ (**3a**) (504 mg, 78%) m.p. 180–182°C. [Found: C, 61.20; H, 3.81; N, 5.09%; *M* (mass spectrometry)

729. $C_{41}H_{30}N_3O_2PRu.CH_2Cl_2$ calcd.: C, 61.99; H, 3.96; N, 5.16%; *M* 729].

Infrared (Nujol): $\nu$(CN) 2222s, 2216s; $\nu$(C=C) 1588s; other bands at 1513s, 1488(sh), 1480m, 1437s, 1354(sh), 1342s, 1114m, 1090s, 852m, 839m, 829m, 817m, 790m, 769m, 754m, 749s, 745(sh), 732s, 708(sh), 700s, 695s, 686m $cm^{-1}$. $^1H$ NMR $\delta(CDCl_3)$: 7.91, 7.80, 6.75, 6.64 (s, 4H, $C_6H_4$), 7.68–7.03 (m, 20H, Ph), 5.29 (s, 2H, $CH_2Cl_2$), 4.66 (s, 5H, $C_5H_5$), 3.10 (d, *J*(HP) 15 Hz, 1H, *H*CPh). $^{13}C$ NMR $\delta(CDCl_3)$: 227.7 (d, *J*(CP) 15 Hz, C(3)), 118.4, 118.2 (s, CN), 150.8, 145.1, 136.6, 128.4, 122.98 (m, Ph), 88.3 (s, $C_5H_5$), 71.8 (s, C(4)), 53.5 (s), 48.8 (s, C(1)C(2)).

*(b) With* $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$. To a stirred solution of $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (144 mg, 0.20 mmol) in toluene (30 ml) was added the olefin (44.0 mg, 0.22 mmol). The reactants were heated in refluxing toluene for 4 h, producing a dark orange solution. Crystallisation by addition of light petroleum and evaporation, and recrystallisation (dichloromethane/hexane) gave dark orange crystals of $Ru[\eta^3\text{-}CH(C_6H_4NO_2)C(Me)C{=}C(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)\cdot 0.5CH_2Cl_2$ (**3b**) (111 mg, 84%), m.p. 221–223°C. [Found: C, 61.09; H, 4.21; N, 5.84%; *M*–$PPh_3$ (mass spectrometry), 405. $C_{36}H_{28}N_3O_2PRu\cdot 0.5CH_2Cl_2$ calcd.: C, 61.86; H, 4.21; N, 5.92%; *M*, 667].

Infrared (Nujol): $\nu$(CN) 2219s, 2210(sh); $\nu$(C=C) 1590s, 1570m; other bands at 1507s, 1493m, 1440m, 1435s, 1340s, 1212(sh), 1208w, 1112(sh), 1110m, 1090m, 1085m, 832m, 748m, 703(sh), 700m, 692m $cm^{-1}$. $^1H$ NMR $\delta(CDCl_3)$: 8.10, 7.99, 7.10, 6.98 (s, 4H, $C_6H_4$), 7.65–7.22 (m, 15H, Ph), 5.29 (s, 1H, $CH_2Cl_2$), 4.62 (s, 5H, $C_5H_5$), 2.87 (d, *J*(HP) 15 Hz, 1H, *H*CPh), 2.22 (s, 3H, $CH_3$).

*(c) With* $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$. A stirred mixture of $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (153 mg, 0.27 mmol) and $C(CN)_2{=}CH(C_6H_4NO_2\text{-}4)$ (55.7 mg, 0.28 mmol) in toluene (30 ml) was heated at reflux point for 18 h. Evaporation to dryness and recrystallisation (twice) from dichloromethane/hexane yielded yellow crystals of the cycloadduct **2c** (153 mg, 74%), m.p. 187–190°C. [Found: C, 65.94; H, 3.89; N, 6.09; *M* (mass spectrometry), 757. $C_{42}H_{30}N_3O_3PRu$ calcd.: C, 66.54; H, 3.99; N, 5.54%; *M*, 757].

Infrared (Nujol): $\nu$(CN) 2240w, 2216m; $\nu$(CO) 1962s; $\nu$(C=C) 1610w, 1594m, 1585m, 1535(sh), 1522s, 1510(sh); other bands at 1440m, 1345s, 1322m, 1306m, 1262m, 1112m, 1092m, 852m, 814m, 748m, 742(sh), 712(sh), 698m $cm^{-1}$. $^1H$ NMR $\delta(CDCl_3)$: 7.94, 7.83, 6.97, 6.86 (s, 4H, $C_6H_4$), 7.52–7.12 (m, 20H, Ph), 5.26 (s, 1H, *H*CPh), 4.74 (s, 5H, $C_5H_5$). An additional peak at $\delta$4.81 ppm is assigned to the $C_5H_5$ resonance of the cyclobutenyl precursor. After 0.5 h this signal had disappeared.

*(d) With* $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$. A mixture of $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)\cdot EtOH$ (170 mg, 0.24 mmol) and $C(CN)_2{=}CH(C_6H_4NO_2\text{-}4)$ (57.0 mg, 0.29 mmol) in toluene (20 ml) was heated at reflux point for 18 h. Evaporation to dryness gave a residue which on crystallisation (dichloromethane/hexane) gave red crystals of the cycloadduct **2d** (192 mg, 88%), m.p. 186–188°C. [Found: C, 66.68; H, 4.77; N, 4.60%; *M*–$PPh_2$ (mass spectrometry), 680. $C_{49}H_{39}N_3O_2P_2Ru\cdot C_2H_5OH$ calcd.: C, 67.22; H, 4.87; N, 4.61%, *M*, 865]. Infrared (Nujol): $\nu$(CN) 2208s, 2198s; $\nu$(C=C) 1609m, 1594s, 1574m, 1518s; other bands at 1494(sh), 1489m, 1437s, 1432s, 1424m, 1420m, 1345s, 1342s, 1110m, 1100m, 1088m, 850m, 832m, 818m, 812(sh), 802m, 792m, 745s, 733m, 710s, 700s, 690s(br) $cm^{-1}$. $^1H$ NMR $\delta(CDCl_3)$: 7.97, 7.88, 7.13, 7.02 (s, 4H, $C_6H_4$), 7.38 (m, 25H, Ph) 4.40 (s, 5H, $C_5H_5$), 3.46 (q, 2H, $CH_2$ of EtOH), 2.38 (m, 4H, $CH_2$), 1.18 (t, 3H, Me of EtOH); vinyl proton not detected.

### *Reactions of* $C(CN)_2{=}CHPh$

*(a) With* $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. A stirred mixture of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (280 mg, 0.35 mmol) and $C(CN)_2{=}CHPh$ (54.2 mg, 0.36 mmol) was heated in refluxing toluene (40 ml) for 18 h. After partial evaporation of the solvent, a yellow compound precipitated from solution. On the basis of IR and m.p. this was confirmed as $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (191 mg, 68%). The remaining brown coloured solution was evaporated to dryness. Extraction of the residue into dichloromethane (ca. 2 ml) and thin layer chromatography on silica (1/1 acetone/light petroleum) showed six bands. Work-up of the major band ($R_f = 0.34$) and recrystallisation from dichloromethane/light petroleum afforded orange-yellow crystals of $Ru[\eta^3\text{-}CHPhC(Ph)C{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)\cdot 0.5CH_2Cl_2$ (**3e**) (36 mg, 14%), m.p. 218–220°C. [Found: C, 69.37; H, 4.52, N, 3.92. $C_{41}H_{31}N_2PRu\cdot 0.5CH_2Cl_2$ calcd.: C, 68.64; H, 4.44; N, 3.86%]. Infrared (Nujol): $\nu$(CN) 2216s, 2204s; $\nu$(C=C) 1570s; other bands at 1479m, 1438m, 1092m, 1085m, 742m, 740(sh), 698s $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$: 7.76–7.17 (m, 25H, Ph), 5.29 (s, 1H, $CH_2Cl_2$), 4.61 (s, 5H, $C_5H_5$), 3.16 (d, $J$(HP) 15 Hz, 1H, *H*CPh).

*(b) With* $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$. A stirred mixture of $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (106 mg, 0.19 mmol) and $C(CN)_2{=}CHPh$ (35.2 mg, 0.23 mmol) in toluene (30 ml) was heated at reflux for 18 h. After evaporation to dryness, crystallisation (dichloromethane/hexane) yielded pale yellow crystals of the cycloadduct (**1f**) (109 mg, 81%), m.p. 229–232°C. [Found: C, 69.26; H, 4.39; N, 3.79%, *M* (mass spectrometry), 712. $C_{42}H_{31}N_2OPRu\cdot 0.5CH_2Cl_2$ calcd.: C, 67.78; H, 4.28; N, 3.71%; *M*, 712]. Infrared (Nujol): $\nu$(CN) 2214 m; $\nu$(CO) 1968s; $\nu$(C=C) 1600 w, 1590vw, 1578w; other bands at 1491m, 1482m, 1445s, 1438m, 1432m, 1160m, 1110m, 1092m, 1088m, 1065m, 1024m, 1005(sh), 1000w, 866m, 856m, 849m, 818m, 804m, 768m, 760m, 750s, 709s, 699s $cm^{-1}$. $^1H$ NMR: $\delta(CDCl_3)$: 7.49–6.87 (m, 25H, Ph), 5.43 (s, 1H, *H*CPh), 5.28 (s, 1H, $0.5CH_2Cl_2$), 4.70 (s, 5H, $C_5H_5$).

### *Reactions of* $CH(C_6H_4NO_2\text{-}4){=}C(CN)(CO_2Et)$

*(a) With* $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. To a stirred solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (165 mg, 0.21 mmol) in toluene (30 ml) was added $CH(C_6H_4NO_2\text{-}4){=}C(CN)CO_2Et$ (49.7 mg, 0.20 mmol). After heating at reflux for 18 h, the colour of the solution had changed from yellow to dark brown. Evaporation to dryness and chromatography by TLC (1/1 acetone/light petroleum) of a dichloromethane extract afforded nine bands. The major band was extracted with acetone, and on the basis of m.p. and IR was found to be recovered $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$.

*(b) With* $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$. A solution of $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (156 mg, 0.21 mmol) and $CH(C_6H_4NO_2\text{-}4){=}C(CN)CO_2Et$ (51.1 mg, 0.21 mmol) in toluene was heated at reflux for 4 h. After evaporation to dryness, crystallisation (dichloromethane/hexane) yielded orange crystals of cycloadduct (**3g**) (129 mg, 62%), m.p. > 244°C (dec.). [Found: C, 63.44; H, 4.76; N, 3.88; $C_{38}H_{33}N_2O_4PRu$ calcd.: C, 63.95; H, 4.66; N, 3.93%]. Infrared (Nujol): $\nu$(CN) 2216s; $\nu$(CO) 1728s, 1715s, 1630m, 1624m, 1618m; $\nu$(C=C) 1601 m, 1591s, 1508s; other bands at 1495m, 1490m, 1435m, 1378m, 1368m, 1340s, 1260s(br), 1111m, 1094(sh), 1090m, 1030m, 808m, 760m, 750s, 699 $cm^{-1}$. $^1H$ NMR $\delta$ $(CDCl_3)$: 8.05, 7.95, 7.08, 6.97; s, 4H, $C_6H_4$; 7.38–7.25 (m, 15H, Ph), 4.60 (s, 5H, $C_5H_5$), 4.14, 412 (q, $J$(HH) 6.8 Hz, 2H, $CH_2CH_3$), 2.92 (d, $J$(HP) 14 Hz, 1H, *H*CPh), 2.25, 2.19 (s, 3H, Me), 1.23 (t, $J$(HH) 6.8 Hz, 3H, $CH_2CH_3$).

*(c) With $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$.* A stirred mixture of $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (149 mg, 0.27 mmol) and $CH(C_6H_4NO_2\text{-}4){=}C(CN)CO_2Et$ (63.2 mg, 0.27 mmol) in toluene (25 ml) was refluxed for 18 h. After the yellow solution was evaporated to dryness, TLC (1/1 dichloromethane/light petroleum) of a dichloromethane extract showed only one product. However, extraction with acetone and crystallisation from hexane gave pale yellow crystals and bright yellow crystals. The bright yellow crystals were separated and recrystallised from dichloromethane/hexane yielding orange crystals of the cycloadduct **2h** (84 mg, 40%), m.p. 208–211°C. [Found: C, 64.38; H, 4.32; N, 3.39%; *M*–Ph (mass spectrometry), 542. $C_{44}H_{35}N_2O_5PRu$ calcd.: C, 65.75; H, 4.39; N, 3.49%; *M* 804.] Infrared (Nujol): $\nu$(CN) 2200m; $\nu$(CO) 1955s, 1728m, 1724(sh), 1695m; $\nu$(C=C) 1610w, 1592m, 1588(sh), 1515(sh), 1510s; other bands at 1485(sh), 1438s, 1380s, 1370m, 1347s, 1227s, 1111m, 1098m, 1088m, 890m, 860m, 835m, 821m, 809m, 793m, 756m, 750m, 704(sh), 697s, 685 $cm^{-1}$. $^1H$ NMR $\delta(CDCl_3)$: 7.91, 7.80, 6.95, 6.85 (s, 4H, $p\text{-}C_6H_4$), 7.46–7.23 (m, 20H, Ph), 4.99 (s, 1H, *H*CPh), 4.68 (s, 5H, $C_5H_5$), 3.71 (q, *J*(HH) 7.2 Hz, 2H, $CH_2CH_3$), 1.25 (t, *J*(HH) 7.2 Hz, 3H, $CH_2CH_3$). $^{13}H$ NMR $\delta(CDCl_3)$: 205.2 (d, *J*(CP) 20.9 Hz, C(3)), 145.7–122.9 (m, Ph), 117.2 (s, CN), 87.63 (s, $C_5H_5$), 60.46 (m, $CH_2$), 14.03 (m, $CH_3$).

### *Crystallography*

Intensity data for a well-formed crystal were measured at 295 K with Mo-$K_\alpha$ (graphite monochromator) radiation on an Enraf–Nonius CAD-4 diffractometer using the $\omega$-$2\theta$ scan technique. A total of 7846 reflections were measured of which 5854 were unique and 4291 satisfied the $I > 2.5\sigma(I)$ criterion of observability. No significant decomposition of the crystal occurred during the data collection and the intensity data were corrected for Lorentz and polarization effects using SUSCAD [6].

*Crystal data.* $C_{49}H_{39}N_3O_2P_2Ru \cdot 0.5CH_2Cl_2$, *M* 907.4, monoclinic, space group $C2/c$ ($C^6_{2h}$, No. 15), *a* 28.81(1), *b* 9.661(2), *c* 30.782(8) Å, $\beta$ 95.02(3)°, *U* 8536.0 Å$^3$, $D_m$ 1.41, $Z = 8$, $D_c$ 1.412 g $cm^{-3}$, Mo-$K_\alpha$ (graphite monochromator) radiation, $\lambda$ 0.7107 Å, $1° \leqslant \theta \leqslant 25°$, $\mu$ 5.02 $cm^{-1}$, $F(000) = 3728$ electrons. The structure was solved initially in the $C2/c$ space group and the interpretation of the Patterson synthesis enabled the location of the Ru atom; all non-hydrogen atoms were located from subsequent difference maps. The phenyl rings were refined as hexagonal rigid groups and anisotropic thermal parameters were introduced for all remaining atoms. Hydrogen atoms were included in the model at their calculated positions. After the introduction of a weighting scheme, $2.4/[\sigma^2(F) + 0.001|F|^2]$, the refinement converged with final *R* and $R_w$ 0.075 and 0.076, respectively. The max. residual electron density peak in the final difference map was 1.13 e Å$^{-3}$ located in the vicinity of the Ru atom. The analysis of variance showed no special features.

The relatively high value of the *R*-index prompted the examination of the structure in the *Cc* space group with two molecules in the asymmetric unit. This model was discarded, however, as a result of gross correlation effects and higher values of *R* and $R_w$. The choice of $C2/c$ as the true space group was supported by the examination of the *E*-statistics. The diffuse nature of the solvent $CH_2Cl_2$ molecule may account for the relatively high *R*-indices. Structure solution and refinement were performed using the SHELX program [6].

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