Selective Preparation of Unusual π-adducts of the Functional Arenes Diphenylacetylene, Phenol, and Benzoic Acid with the $CpRu^+$ Fragment (Cp = C_5Me_5)

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Protonation of $[CpRu(OMe)]_2$ (**1**) with CF_3SO_3H in tetrahydrofuran (THF) in the presence of methanol yields $[CpRu(MeOH)_3](CF_3SO_3)$ (**2**); (**2**) or the reaction mixture (**1**) + CF_3SO_3H reacts with one or half an equivalent of diphenylacetylene, benzoic acid, and phenol to give, respectively, $[CpRu(\eta^6\text{-}PhC{\equiv}CPh)](SO_3CF_3)$ (**3**), $[(CpRu)_2(\eta^6, \eta^6\text{-}PhC{\equiv}CPh)](SO_3CF_3)_2$ (**4**), $[CpRu(\eta^6\text{-}PhCO_2H)](SO_3CF_3)$ (**6**), and $[CpRu(\eta^6\text{-}PhOH)](SO_3CF_3)$ (**8**), whereas the direct reactions of (**1**) with phenol and benzoic acid yield, respectively, $[CpRu(\eta^5\text{-}PhO)]$ (**7**) and the zwitterionic derivative $[CpRu(\eta^6\text{-}PhCO_2)]$ (**5**); the facile interconversion (**5**)← →(**6**) and (**7**)← →(**8**) was demonstrated by ^1H NMR.

Cationic cyclopentadienyl Group VIII fragments show a strong affinity for arenes. This is especially true for ruthenium derivatives,[1] but it is only recently that such compounds containing the C_5Me_5 (Cp) ligand have been prepared.[1—4] We have achieved a facile preparation of such π-arene derivatives based on zinc reduction in tetrahydrofuran (THF) of $[CpRuCl_2]_n$,[4] a readily available starting material.[5] However problems arise in scaling up the reaction, the main one being the deposition of the ruthenium complex on zinc. An alternative preparation of such derivatives has recently been reported and applied to the synthesis of new conducting materials.[1] This method requires three steps and the isolation of intermediates.

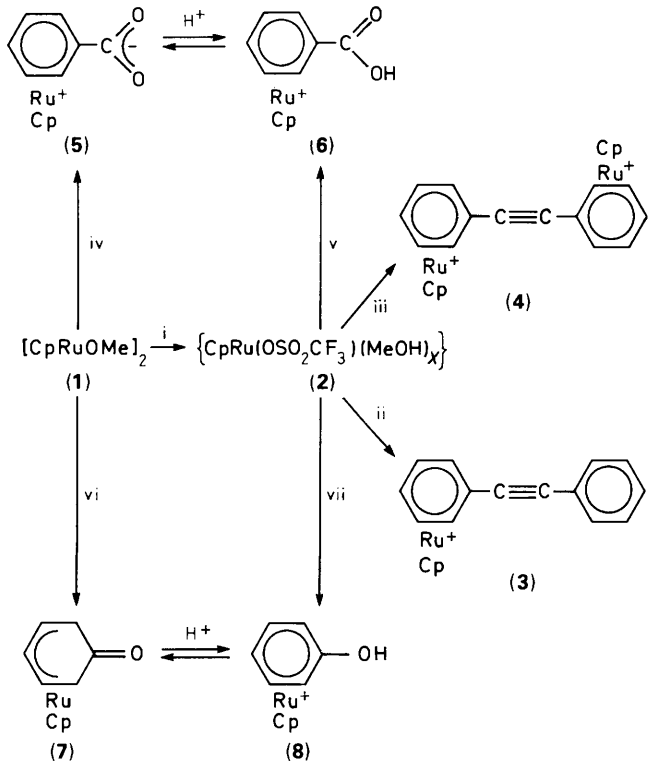
We have previously reported that the 'CpRu$^+$' fragment leads to π-complexes with heterocycles possessing bifunctionality (*i.e.* the aromatic ring + heteroatom lone pair), the best examples being pyridine or 3,5-lutidine.[4,6] It was of interest to determine whether this selectivity could be generalized to aromatic organic derivatives which would normally bind through a functionality different from the aromatic ring.

This communication describes a new convenient method for the preparation of π-arene derivatives based on the protonation of $[CpRu(OMe)]_2$ and its application to the preparation of unusual π-adducts of diphenylacetylene, phenol, and benzoic acid.

Koelle *et al.* have reported a convenient nearly quantitative one step synthesis of $[CpRu(OMe)]_2$ (**1**) from $[CpRuCl_2]_n$ and K_2CO_3 in MeOH.[3] We found that (**1**) is very reactive towards acids leading to methanol elimination and formation of new derivatives. The reaction of (**1**) with CF_3SO_3H leads to an immediate colour change from deep cherry-red to red–brown. When the reaction was carried out in THF in the presence of methanol, $[CpRu(MeOH)_3](OSO_2CF_3)$ (**2**) was isolated. The reaction proceeds similarly in CH_2Cl_2 or THF but no defined complex was isolated.

Complex (**2**) [or the reaction mixture of (**1**) plus (CF_3SO_3H)] reacts immediately with aromatics to give π-adducts. As a comparison to earlier work, reaction with thiophene was shown to lead to higher yields of $CpRu(\eta^5\text{-}C_4H_4S)CF_3SO_3$ (*ca.* 80% crystallized product).

Reaction of 1.0 or 0.5 equiv. of diphenylacetylene with (**2**) yields, respectively, $[CpRu(\eta^6\text{-}Ph\text{–}C{\equiv}C\text{–}Ph)]CF_3SO_3$ (**3**) and $[(CpRu)_2(Ph\text{–}C{\equiv}C\text{–}Ph)](CF_3SO_3)_2$ (**4**). Both compounds are thermally- and air-stable. As expected, the IR spectrum of (**3**) shows a $\nu_{C\equiv C}$ stretch at 2227 cm^{-1} whereas that of (**4**) does not. Similarly, the ^1H NMR spectrum of (**3**) shows a 1 : 1 ratio of co-ordinated phenyl protons (δ 6.1—6.4) to free phenyl protons (δ 7.1—7.5) whereas that of (**4**) shows only resonances for coordinated protons. The structure of (**4**) was ascertained by an *X*-ray crystal structure determination which will be described in detail in a subsequent full paper. In neither of the two compounds is the C≡C triple bond involved in co-ordination, a very rare observation in organometallic chemistry. Furthermore, the C≡C distance is 1.147 (9) Å and is not elongated but slightly shortened relative to a normal C≡C distance (1.20 Å).



Scheme 1. Reactions of $[CpRu(OMe)]_2$ (**1**) with functional arenes in the presence or absence of CF_3SO_3H. *Reagents and conditions*: i, $HOSO_2CF_3$; ii, PhC≡CPh; iii, 1/2PhC≡CPh; iv, −MeOH, $PhCO_2H$; v, $PhCO_2H$; vi −MeOH, PhOH; vii, PhOH.

An even more surprising reaction was found with benzoic acid. Thus, (**1**) reacts instantly with $PhCO_2H$ to give the white crystalline neutral $CpRu(\eta^6\text{-}PhCO_2)$ (**5**). The NMR data are again indicative of π-co-ordination of the aromatic ring. The analogous $[CpRu(\eta^6\text{-}PhCO_2H)](OSO_2CF_3)$ (**6**) can be prepared from (**2**) and benzoic acid. The IR spectrum of (**6**) shows a C=O band at 1720 cm^{-1}, at higher frequency than that found for (**5**) (1600 cm^{-1}) and a characteristic absorption for a hydrogen-bonded OH group at 3085 cm^{-1}. The structure of (**6**) is thus presumably dimeric. Complex (**6**) results formally from the protonation of (**5**). The interconversion

$$(5) \underset{NEt_3}{\overset{CF_3SO_3H}{\rightleftharpoons}} (6) \qquad (1)$$

Table 1. ^{1}H NMR chemical shifts (δ) of the products (**2**—**8**) in $(CD_3)_2CO$ at 200.133 MHz.

Compound	Cp	Co-ordinated arene	Others
$[CpRu(MeOH)_3](CF_3SO_3)$ (**2**)	1.97 (s, 15H)		2.89 (s, 9H)[a]
$[CpRu(\eta^6\text{-PhC}\equiv\text{CPh})](SO_3CF_3)$ (**3**)	2.18 (s, 15H)	6.35 (m, 5H)	7.77 (m, $2H_m$)[b]
			7.61 (m, $3H_o$ and H_p)[b]
$[CpRu)_2(\eta^6,\eta^6\text{-PhC}\equiv\text{CPh})](SO_3CF_3)_2$ (**4**)	2.20 (s, 15H)	6.53 (m, $2H_m$)	
		6.38 (m, $3H_o$ H_p)	
$[CpRu(\eta^6\text{-PhCO}_2)]$ (**5**)	2.07 (s, 15H)	6.50 (m, $2H_m$)	
		6.02 (m, $3H_o$ H_p)	
$[CpRu(\eta^6\text{-PhCO}_2H)](SO_3CF_3)$ (**6**)	2.13 (s, 15H)	6.62 (m, $2H_m$)	
		6.29 (m, $3H_o$ H_p)	
$[CPRu(\eta^6\text{-PhO}^5)]\cdot 2PhOH$ (**7**)	2.0 (s, 15H)	5.46 (dd,[d] $2H_m$)	7.26 (m, $2H_m$)[c]
		5.27 (t,[e] $1H_p$)	6.98 (m, $2H_o$)[c]
		4.96 (d,[f] $2H_o$)	6.86 (m, $1H_p$)[c]
$[CpRu(\eta^6\text{-PhOH})](SO_3CF_3)$ (**8**)	2.16 (s, 15H)	6.02 (m, $4H_m$ H_o)	
		5.88 (m, $1H_p$)	

[a] Methanol co-ordinated. [b] Unco-ordinated arene. [c] Free phenol. [d] $J_{HH'}$ = 5.3 Hz, $J_{HH''}$ = 6.5 Hz. [e] $J_{HH'}$ = 5.3 Hz. [f] $J_{HH'}$ = 6.5 Hz.

Table 2. ^{13}C NMR chemical shifts (δ) of the products (**3**—**8**) in $(CD_3)2CO$.

Compound	C_5Me_5	$C_5\mathit{Me}_5$	Co-ordinated arene	Others
(**3**)[a]	97.63 (s)	8.24 (q, *J* 128.84 Hz)	91.41 (s)	132.34 (d, *J* 152.15 Hz)[e]
			89.87 (d), *J* 183.58 Hz)	130.24 (d, *J* 162.30 Hz)[e]
			87.89 (d), *J* 182.58 Hz)	129.17 (d, *J* 147.08 Hz)[e]
			87.80 (d), *J* 182.58 Hz)	121.31 (s)
				85.35 (s), *C'*≡C, 83.37 (s), C≡*C'*
(**4**)[a]	98.05 (s)	9.71 (q *J* 119.03 Hz)	90.13 (d, *J* 179.97 Hz)	85.62 (s), C≡C
			88.11 (d, *J* 179.97 Hz)	
			85.86 (d, *J* 179.97 Hz)	
			83.16 (s)	
(**5**)[b]	95.79 (s)	9.54	88.67	
			87.49	
			87.22	
(**6**)[c]	97.74	9.55	89.15	
			88.61	
			87.91	
(**7**)[a]	91.77	9.96 (q, *J* 128.68 Hz)	149.04 (s)	158.71 (s)[f]
			86.66 (d, *J* 169.53 Hz)	129.38 (d, *J* 159.84 Hz)[f]
			78.80 (d, *J* 173.70 Hz)	118.57 (d, *J* 142.56 Hz)[f]
			78.12 (d, *J* 166.53 Hz)	115.67 (d, *J* 157.75 Hz)[f]
(**8**)[d]	95.69 (s)	9.77 (q, *J* 128.62 Hz)	130.67 (s)	
			86.44 (d, *J* 177.79 Hz)	
			84.45 (d, *J* 177.54 Hz)	
			77.44 (d, *J* 175.06 Hz)	

[a] At 50.324 MHz. [b] At 61.896 MHz {^{1}H}BB. [c] At 50.324 MHz {^{1}H}BB. [d] At 61.896 MHz. [e] Unco-ordinated arene. [f] Free phenol.

was verified by NMR. Complex (**5**) is zwitterionic and represents a rare example of such a stabilized carboxylato derivative [reaction (1)].

Finally, a weaker acid such as phenol (excess) also reacts with (**1**) to give the white crystalline $[CpRu(\eta^5\text{-PhO})]\cdot 2(PhOH)$, (**7**). The related derivative $RuH(\eta^5\text{-PhO})(PPh_3)_2\cdot 2(PhOH)$ has previously been reported by Wilkinson.[8] The ease of the preparation of (**7**) is surprising and suggests a large number of possible reactions with weak acids. The reaction of (**2**) with phenol leads to $[CpRu(\eta^6\text{-PhOH})](CF_3SO_3)$ (**8**), in high yield. The comparison of the ^{1}H NMR spectra of (**7**) and (**8**) is interesting. Thus (**8**) shows the *para* hydrogens (H_p) of phenol at δ 5.88 (t) and the *ortho* and *meta* hydrogens (H_o and H_m respectively) at δ 6.01 (d) and 6.06 (t), respectively. In the case of (**7**), the *para* and *meta* hydrogen signals appear at δ 5.27 (t) and 5.46, respectively, while the *ortho* resonance moves to higher field and appears at δ 4.96 (dd). The larger shift of the *ortho* hydrogens is most probably related to the deformation of the aromatic ring which becomes a cyclohexadienylone ligand.

A single mean signal is observed in ^{1}H NMR for the aromatic proton of the π-co-ordinated phenol rings in a mixture of (**7**) + (**8**) with the stoicheiometries 1:2, 2:1 and 1:1.† In the latter case, ^{1}H NMR spectra of the mixture have been recorded at variable temperature, from 303 to 183 K. This demonstrates the very low activation barrier to proton exchange between (**7**) and (**8**) and thus the ease of deformation of the phenyl ring in this system.

As a whole, this study demonstrates the selectivity of the co-ordination of the '$CpRu^+$' fragment to arenes, even in the presence of potentially better co-ordinating groups like acetylene or carboxylic acid. Compounds (**3**)—(**6**) are, to the best of our knowledge, the first examples of such observa-

† *Selected spectra*; ^{1}H NMR (200.133 MHz), CD_2Cl_2: stoicheiometry (**7**):(**8**) = 1:2, δ 5.26 (t.t, $1H_p$), 5.43 (m, $2H_m$, $2H_o$); (**7**):(**8**) = 1:1, δ 5.18 (5, $1H_p$), 5.35 (m, $2H_m$, $2H_o$); (**7**):(**8**) = 2:1, δ 5.11 (t, $1H_p$), 5.20 (d, $2H_o$), 5.30 (t, $2H_m$).

tions. Furthermore the preparation of the zwitterionic complex (**5**) may lead to interesting physical properties.

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References

1 See P. J. Fagan, M. D. Ward, and J. Calabrese, *J. Am. Chem. Soc.*, 1989, **111**, 1698 and references cited therein.
2 A. M. McNair, D. C. Boyd, and K. R. Mann, *Organometallics*, 1986, **5**, 303; A. M. McNair and K. R. Mann, *Inorg. Chem.*, 1986, **25**, 2519; J. L. Schrenk, A. M. McNair, F. M. McCormick, and K. R. Mann, *Inorg. Chem.*, 1986, **25**, 3501.
3 U. Koelle and J. Kossakowski, *J. Chem. Soc., Chem. Commun.*, 1988, 549.
4 B. Chaudret and F. Jalon, *J. Chem. Soc., Chem. Commun*, 1988, 711.
5 T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, *Organometallics*, 1984, **3**, 274; N. Oshima, H. Suzuki, and Y. Moro-Oka, *Chem. Lett.*, 1984, 1161.
6 B. Chaudret, F. Jalon, M. Perez-Manrique, F. J. Lahoz, F. J. Plou, and R. Sanchez-Delgado, *Nouv. J. Chem.*, in the press.
7 B. Chaudret, F. Dahan, X. D. He, and Y. S. Huang unpublished results.
8 D. J. Cole-Hamilton, R. J. Young, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 1995.