Ring-Methyl Activation in Pentamethylcyclopentadienyl Complexes. 8.[1] Introduction of Organic Functionalities at Substituted Tetramethylcyclopentadienyl Complexes of Ruthenium(II)

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A series of complexes derived from nucleophilic attack at the CH_2Cl of [(η^5-$C_5Me_4CH_2Cl$)-$Ru(CO)_2Cl$], **1**, by a wide variety of organic reagents are described. Most reactions proceed in good yield and do not appear to affect the $Ru(CO)_2Cl$ group, even though they are performed under quite stringent (oxidizing, acidic, or hydrolytic) conditions. Hydrolysis of **1** in the presence of collidine gives the alcohol complex, [($C_5Me_4CH_2OH$)$Ru(CO)_2Cl$], **2**, which is oxidized (Me_2SO, oxalyl chloride) to [(C_5Me_4CHO)$Ru(CO)_2Cl$], **4a**, and which can be further oxidized ($KMnO_4$) to [($C_5Me_4CO_2H$)$Ru(CO)_2Cl$], **10**. The alcohol complex **2** forms esters [($C_5Me_4CH_2O_2CR$)$Ru(CO)_2Cl$], **3** (R = Me, CH_2=CH, 2-furyl, and 2-thienyl), on reaction with $RCOCl/Et_3N$. The aldehyde **4a** is a very versatile starting material: It forms acetals such as [($C_5Me_4CH(OCH_2)_2$)$Ru(CO)_2Cl$], **5a**, with ethylene glycol. It reacts with phenylhydrazine and *p*-toluidine in the presence of acid to give [(C_5Me_4CH=NNHPh)$Ru(CO)_2Cl$], **6**, and [(C_5Me_4CH=N-*p*-To)$Ru(CO)_2Cl$], **7**. It also reacts with carbon nucleophiles such as PhMgBr to give [($C_5Me_4CH(OH)Ph$)$Ru(CO)_2Cl$], **8a**, with lithium enolates to give [($C_5Me_4CH(OH)R$)-$Ru(CO)_2Cl$], **8b**−**d** (R = 2-oxocyclohexyl, $MeCOCH_2$, and $PhCOCH_2$), and with Wittig reagents to give [(C_5Me_4CH=CHR)$Ru(CO)_2Cl$], **9** (R = $EtCO_2$, Ph, MeCO, and PhCO). The carboxylic acid **10** forms the acid chloride [(C_5Me_4COCl)$Ru(CO)_2Cl$], which reacts with diisopropylamine to give the amide [($C_5Me_4CON(i\text{-}Pr)_2$)$Ru(CO)_2Cl$], **12**. The structures of complexes [($C_5Me_4CH(OH)Ph$)$Ru(CO)_2Cl$], **8a,** [($C_5Me_4CH(OH)CH_2COPh$)$Ru(CO)_2Cl$], **8d,** and [(*E*-C_5Me_4CH=CHPh)$Ru(CO)_2Cl$], **9b,** have been confirmed by X-ray determinations.

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Introduction

Since the more highly substituted cyclopentadienyls generally form more inert bonds to metals than η^5-C_5H_5 itself, their complexes are more interesting as potential catalysts since ring loss during the catalytic cycle is less of a problem. Our aim in this work has been to synthesize complexes bearing *permethyl*cyclopentadienyl ligands, η^5-C_5Me_4R, where R is a pendant arm bearing a functionality which can act as a *hand* to grasp, orient, and hold potential reactants to the metal in such a way that stereospecific reactions ensue. The elaboration and hence the reactivity of these hand substituents when complexed to the metal are also of importance.

Such metal complexes can be made either by reaction of the permethylcyclopentadiene (or permethylcyclopentadienyl) already bearing the substituent R with a suitable metal salt or by the functionalization of a metal pentamethylcyclopentadienyl complex. The first route has the disadvantages that suitably substituted and functionalized permethylcyclopentadienyls are often hard to make and that, in attaching them to the metal, reagents (e.g. *n*-BuLi) often need to be used which do not tolerate some functionalities which one would like to use as hands.

We have therefore been examining ways of functionalizing pentamethylcyclopentadienyl rings and have previously described simple syntheses of substituted tetramethylcyclopentadienyl complexes of ruthenium(II), of the type [(η^5-$C_5Me_4CH_2X$)$Ru(CO)_2Cl$].[2] The parent complex, [(η^5-$C_5Me_4CH_2Cl$)$Ru(CO)_2Cl$], **1**, is readily made in a two-step, one pot, reaction from [{η^5-$C_5Me_5RuCl_2$}$_2$].[3,4] The $-CH_2Cl$ group in complex **1** has high reactivity toward nucleophiles such as alcohols and amines,[2] leading to C−O and C−N bonds, and it can even react as an electrophile toward arenes in Friedel−Crafts reactions, giving C−aryl bonds.[5] Since the remainder of the molecule is unreactive toward these reagents, they allow transformations at the $-CH_2Cl$ without affecting the $Ru(CO)_2Cl$. As the $Ru(CO)_2Cl$ can be modified in other ways, for example reaction of [{η^5-$C_5Me_5CH_2OMe$}$Ru(CO)_2Cl$] with NaX gives [{η^5-$C_5Me_4CH_2OMe$}$Ru(CO)_2X$],[2] this opens the path to the synthesis of a large range of new complexes.

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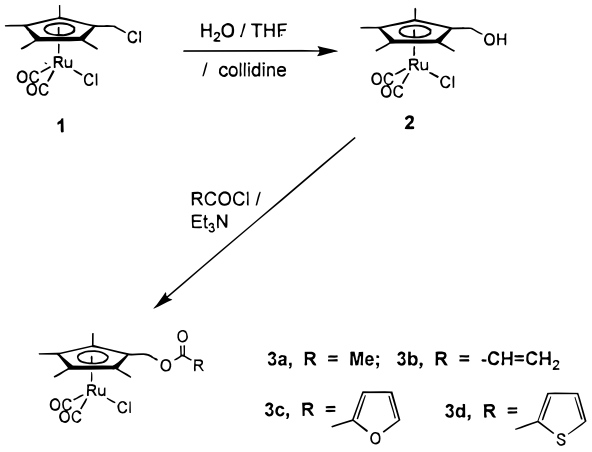
Scheme 1



In general the "soft" nucleophiles (uncharged species such as amines or alcohols) are those that substitute most cleanly at the CH_2Cl, giving C−heteroatom linkages. However since our aim is to make complexes which will act as catalysts, they will require quite robust linkages, preferably with C−C bonds. One way in which to approach this problem is to make the aldehyde; as that is a harder electrophilic center, it should react with harder carbon-based nucleophiles to make carbon−carbon bonds.

That strategy has been followed, and we here report details of new reactions at the ring CH_2 that introduce alcohol, aldehyde, and carboxylic acid functions and their further organic reactions. It may be noted that the reactions have required, inter alia, oxidizing ($KMnO_4$/acetone/40 °C) and reducing (phenyl Grignard) conditions as well as the presence of acids, bases (e.g. lithium enolates), excess chloride, and water; they take place as they do for a purely organic molecule and without affecting the metal or its directly bonded ligands. Furthermore the complexes survive chromatographic workup on silica columns.

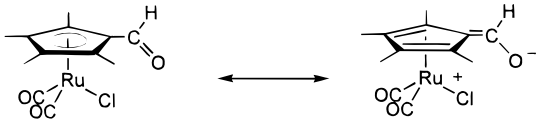
Results and Discussion

Alcohol Complex 2 and Esters 3 Derived from It. We previously described the synthesis of the alcohol (hydroxy) complex **2**, but only in modest yield, by hydrolysis of **1** in aqueous THF in the presence of triethylamine.[2] We have now found that if the weak base collidine is used instead of triethylamine, the alcohol complex is formed nearly quantitatively, thus making it a readily available starting material for further syntheses. The reason for this may lie in the collidine being sufficiently basic to remove the HCl produced but not sufficiently basic to generate appreciable amounts of OH^- which can attack the Ru−Cl.

The alcohol reactions are shown in Scheme 1; complex **2** reacts with a variety of organic acid chlorides (RCOCl) in CH_2Cl_2 in the presence of triethylamine to give the esters **3** (**a**, R = Me, **b**; CH_2=CH; **c**, 2-furyl; **d**, 2-thienyl) in 65−68% yields. As expected, the spectroscopic data (IR, Table 1, ^{1}H NMR, Table 2, and ^{13}C NMR, Table 3) were almost identical for the four compounds synthesized, and only those signals characteristic of the R group were significantly different.

Aldehyde Complex 4a and Complexes 5−9 Derived from It. Several methods were initially tried to make the aldehyde **4a**, including reaction of the chloride **1** with $NaHCO_3$ in hot Me_2SO[6] and of the alcohol complex **2** with Me_2SO and dicyclohexylcarbodiimide.[7] Although they worked, the aldehyde **4a** was only obtained in very low yields (∼5%), and substantial amounts of starting material were recovered; rather better was the reaction of **2** with Me_2SO and P_2O_5,[8] which gave 28% of **4a**. However, the method of Swern et al.,[9] using Me_2SO and oxalyl chloride, was much more successful and gave the aldehyde in 82% yield. The formation and reactions of the aldehyde are shown in Scheme 2.

The aldehydic CO absorbed at 1684 cm^{-1} in the IR and had properties rather similar to those which had been reported for ferrocenecarboxaldehyde, [η^5-C_5H_5Fe-(η^5-C_5H_4CHO)].[10] That showed ν(CO) at 1671 cm^{-1} down from benzaldehyde ν(CO) at 1703 cm^{-1}. The drop in ν(CO) implies a lower CO bond order and a greater polarization toward $C^{\delta+}-O^{\delta-}$ with the positive charge being stabilized over the whole π-complex, either the ferrocene or Cp*Ru(CO)$_2$Cl. This can be written in the canonical forms for **4a**,



Such a polarization accounts for the solubility of ferrocenecarboxaldehyde in dilute acid; the ruthenium aldehyde complex **4a** shows similar behavior and can be extracted from organic solvents by dilute acid. It is, however, unstable toward aqueous base, probably because OH^- attacks at the Ru. The broad scope of the new chemistry possible for these ruthenium complexes is revealed by the ability to exchange the chloride on ruthenium for bromide, iodide, or thiocyanate **4b**−**d** (Scheme 2) by reaction with the appropriate sodium salt in acetone under very mild conditions. Thus the organic functionality can be introduced in one step and the inorganic functionality changed in a second step. The organic transformations are exemplified by the reactions of **4a** to form acetals, imines, and hydrazones and by its reactions with Grignards, lithium enolates, and Wittig reagents.

On reaction with ethylene glycol in CH_2Cl_2 in the presence of trimethylchlorosilane[11] the cyclic acetal, **5a**, was obtained in good yield; analogous reactions with 1,2- and 1,3-propylene glycol led to the cyclic acetals **5b**,**c**, respectively. The conditions used are the same as are used to form acetals of purely organic aldehydes.

Similarly, the aldehyde **4a** underwent condensation reactions with hydrazines, for example, phenylhydrazine, to give the phenylhydrazone **6**, and with amines, for example, p-toluidine, to give the imine **7**. Both

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Table 1. Yields, IR Spectral Data, and Microanalytical Data

	yield, %	IR (ν(CO), cm^{-1})	C, %[a]	H, %[a]	N, %[a]	other %[a]
[{RuCl}CH_2OH][b] (**2**)	92	1986, 2038				
[{RuCl}CH_2O_2CMe] (**3a**)	65	1741, 1987, 2039	43.6 (43.6)	4.4 (4.4)		
[{RuCl}$CH_2O_2CCH{=}CH_2$] (**3b**)	65	1726, 1987, 2040	45.4 (45.3)	4.3 (4.3)		
[{RuCl}CH_2O_2C(2-furoyl)] (**3c**)	68	1728, 1988, 2040	46.7 (46.6)	3.85 (3.9)		
[{RuCl}CH_2O_2C(2-thienyl)] (**3d**)	67	1712, 1988, 2040	44.5 (45.0)	3.6 (3.8)		S, 7.1 (7.1)
[{RuCl}CHO] (**4a**)	82	1684, 2001, 2051	41.6 (42.2)	3.7 (3.8)		
[{RuBr}CHO] (**4b**)	86	1685, 2001, 2049	37.3 (37.2)	3.4 (3.2)		Br, 20.7 (20.7)
[{RuI}CHO] (**4c**)	85	1684, 1998, 2045	33.3 (34.0)	3.0 (3.1)		I, 29.3 (30.0)
[{RuSCN}CHO] (**4d**)	42	1687, 2007, 2054	42.9 (43.3)	3.6 (3.6)	3.9 (3.9)	S, 8.8 (9.0)
[{RuCl}$CHOCH_2CH_2O$] (**5a**)	92	1988, 2041	43.6 (43.5)	4.4 (4.2)		
[{RuCl}$CHOCHMeCH_2O$] (**5b**)	75	1986, 2040	45.1 (44.8)	4.8 (4.5)		
[{RuCl}$CHOCH_2CH_2CH_2O$] (**5c**)	46	1987, 2041	45.1 (44.6)	4.8 (4.7)		
[{RuCl}$CH{=}NNHPh$] (**6**)	76	1985, 2037	50.1 (49.85)	4.4 (4.3)	6.5 (6.4)	
[{RuCl}CH=N-*p*-To] (**7**)	58	1991, 2043	53.0 (52.8)	4.65 (4.5)	3.25 (3.0)	
[{RuCl}CHPhOH] (**8a**)	76	1988, 2039	51.4 (51.5)	4.3 (4.6)		
[{RuCl}$CH(C_6H_9O)OH$] (**8b**)	41	1699, 1986, 2039	48.9 (49.15)	5.1 (5.3)		
[{RuCl}$CH(CH_2COMe)OH$] (**8c**)	15	1716, 1987, 2039	45.1 (45.1)	4.5 (4.8)		
[{RuCl}$CH(CH_2COPh)OH$] (**8d**)	69	1682, 1987, 2039	52.1 (52.0)	4.6 (4.6)		
[{RuCl}$CH{=}CHCO_2Et$] (**9a**)	60	1711, 1990, 2041	46.3 (46.7)	4.7 (4.65)		
[{RuCl}$CH{=}CHPh$] (**9b**); *Z* isomer	11	1982, 2035	54.7 (54.9)	4.5 (4.6)		
[{RuCl}$CH{=}CHPh$] (**9b**); *E* isomer	21	1982, 2035	54.7 (54.9)	4.5 (4.6)		
[{RuCl}$CH{=}CHCOMe$] (**9c**)	61	1668, 1990, 2041	47.0 (47.2)	4.2 (4.5)		
[{RuCl}$CH{=}CHCOPh$] (**9d**)	16	1667, 1990, 2041	53.6 (54.1)	4.3 (4.3)		
[{RuCl}CO_2H] (**10**)	64	1998, 2049, $\nu(CO_2)$ 1732	39.7 (40.3)	3.9 (3.7)		
[{RuCl}$CON(i\text{-}Pr)_2$] (**12**)	59	1631, 1981, 2035	46.9 (49.0)	6.1 (5.9)	2.9 (3.2)	

[a] Calculated in parentheses. [b] {RuCl} = {(η^5-C_5Me_4−)$Ru(CO)_2Cl$}.

Table 2. ^{1}H NMR Spectra (δ, ppm; $CDCl_3$ Solution)

	C_5Me_4	CHE	E
[{RuCl}CH_2O_2CMe][a] (**3a**)	1.93 (s, 6H), 2.0 (s, 6H)	4.75 (s, 2H)	2.07 (s, Me)
[{RuCl}$CH_2O_2CCH{=}CH_2$] (**3b**)	1.91 (s, 6H), 2.0 (s, 6H)	4.84 (s, 2H)	$CH_2{=}CH-$, 5.87 (dd, 1H), 6.11 (dd, 1H), 6.45 (dd, 1H)
[{RuCl}CH_2O_2C(2-furoyl)] (**3c**)	1.93 (s, 6H), 2.05 (s, 6H)	4.99 (s, 2H)	2-furoyl, 6.51 (dd, 1H), 7.21 (d, 1H), 7.60 (d, 1H)
[{RuCl}CH_2O_2C(2-thienyl)] (**3d**)	1.92 (s, 6H), 2.05 (s, 6H)	4.99 (s, 2H)	2-thienyl, 7.10 (dd, 1H), 7.59 (d, 1H), 7.82 (d, 1H)
[{RuCl}CHO] (**4a**)	2.00 (s, 6H), 2.22 (s, 6H)	9.95 (s, 1H)	
[{RuBr}CHO] (**4b**)	2.03 (s, 6H), 2.33 (s, 6H)	9.91 (s, 1H)	
[{RuI}CHO] (**4c**)	2.11 (s, 6H), 2.46 (s, 6H)	9.90 (s, 1H)	
[{RuSCN}CHO] (**4d**)	1.99 (s, 6H), 2.25 (s, 6H)	9.92 (s, 1H)	
[{RuCl}$CHOCH_2CH_2O$] (**5a**)	1.87 (s, 6H), 2.02 (s, 6H)	5.51 (s, 1H)	(OCH_2CH_2O), 4.02 (m, 2H), 4.13 (m, 2H)
[{RuCl}$CHOCHMeCH_2O$] (**5b**)	1.83 (s, 6H), 1.98 (s, 6H)	5.48 (s, 1H)	($OCH(Me)CH_2O$), 4.24 (m, 2H), 4.02 (t, 2H), 1.31 (d, Me)
[{RuCl}$CHOCH_2CH_2CH_2O$] (**5c**)	1.82 (s, 6H), 1.97 (s, 6H)	5.10 (s, 1H)	($OCH_2CH_2CH_2O$), 4.14 (dd, 2H), 3.81 (td, 2H), 1.53 (m, 1H), 1.34 (m, 1H)
[{RuCl}$CH{=}NNHPh$] (**6**)	2.16 (s, 6H), 1.97 (s, 6H)		($NNHC_6H_5$), 7.36 (d, 1H), 7.25 (t, 2H), 6.98 (d, 1H), 6.88 (t, 1H)
[{RuCl}CH=N-*p*-To] (**7**)	2.22 (s, 6H), 1.99 (s, 6H)	8.24 (s, 1H)	(NC_6H_4Me), 7.16 (d, 2H), 7.04 (d, 2H), 2.35 (s, Me)
[{RuCl}CHPhOH] (**8a**)	1.89 (s, 3H), 1.94 (s, 3H), 2.07 (s, 6H)	5.67 (d, 1H)	3.81 (d, 1H, OH), 7.36 (m, 5H, phenyl)
[{RuCl}$CH(C_6H_9O)OH$] (**8b**)	1.88 (s, 3H), 1.90 (s, 3H), 1.91 (s, 3H), 2.10 (s, 3H)	4.60 (d, 1H)	1.25−2.75 (m, 9H)
[{RuCl}$CH(CH_2COMe)OH$] (**8c**)	1.92 (s, 3H), 1.93 (s, 3H), 2.00 (s, 3H), 2.14 (s, 3H)	4.94 (ddd, 1H)	3.58 (d, 1H, OH); CH_2, 2.74 (dd, 1H), 3.02 (dd, 1H), 2.24 (s, Me)
[{RuCl}$CH(CH_2COPh)OH$] (**8d**)	1.90 (s, 3H), 1.92 (s, 3H), 2.00 (s, 3H), 2.15 (s, 3H)	5.09 (m, 1H)	phenyl, 7.48 (dd, 2H), 7.59 (dd, 1H), 7.97 (dd, 2H); 3.60 (dd, 1H); CH_2, 3.37 (dd, 1H), 3.74 (d, 1H, OH)
[{RuCl}$CH{=}CHCO_2Et$] (**9a**)	1.96 (s, 6H), 2.06 (s, 6H)		ethyl, 1.33 (t, Me), 4.24 (q, 2H); vinyl, 6.20 (d, 1H; J(H−H) 15 Hz), 7.32 (d, 1H)
[{RuCl}$CH{=}CHPh$] (**9b**); *Z* isomer	1.65 (s, 6H), 1.93 (s, 6H)		vinyl, 6.19 (d, 1H, J(H−H) 11.9 Hz), 6.82 (d, 1H); phenyl, 7.13−7.5 (m, 5H)
[{RuCl}$CH{=}CHPh$] (**9b**); *E* isomer	1.97 (s, 6H), 2.07 (s, 6H)		vinyl, 6.62 (d, 1H, J(H−H) 16.5 Hz), 6.85 (d, 1H); phenyl, 7.13−7.50 (m, 5H)
[{RuCl}$CH{=}CHCOMe$] (**9c**)	1.99 (s, 6H), 2.07 (s, 6H)		vinyl, 6.49 (d, 1H, J(H−H) 15 Hz), 7.18 (d, 1H); Me, 2.34 (s, Me)
[{RuCl}$CH{=}CHCOPh$] (**9d**)	2.01 (s, 6H), 2.14 (s, 6H)		vinyl, 7.32 (d, 1H, J(H−H) 16 Hz), 7.47 (d, 1H); phenyl, 7.54 (m, 3H), 7.98 (m, 2H)
[{RuCl}CO_2H] (**10**)	2.00 (s, 6H), 2.22 (s, 6H)		CO_2H, 3.25 (br, 1H)
[{RuCl}$CON(i\text{-}Pr)_2$] (**12**)	1.89 (s, 6H), 2.20 (s, 6H)		*i*-Pr, 1.34 (d, 4 × Me), 3.28 (sept, 2H)

[a] {RuCl} = {(η^5-C_5Me_4−)$Ru(CO)_2Cl$}.

reactions required the presence of a strong acid as catalyst; it is noteworthy that the phenylhydrazone was formed in 91% yield and there was no reduction of the ruthenium.

The reactions of Grignard reagents with organometallics usually lead to substitution at the metal, especially if a metal−halide bond is present. Thus is very surprising that **4a** reacts with the Grignard phenyl-

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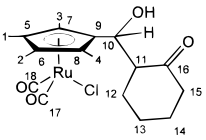
Table 3. ^{13}C NMR Spectra (δ, ppm; $CDCl_3$ Solution)

	C_5Me_4	CO	Me_4C_5CH	E
[{RuCl}$CH_2O_2CCH{=}CH_2$][a] (**3b**)	9.7, 10.15 (C_5Me_4), 89.5, 100.3, 106.6 (C_5Me_4)	197.5	56.8	127.6 ($CO\mathit{C}HCH_2$), 131.9 ($COCH\mathit{C}H_2$), 166.0 ($\mathit{C}OCHCH_2$)
[{RuCl}CH_2O_2C(2-furoyl)] (**3c**)	9.8, 10.2 (C_5Me_4), 89.2, 100.2, 107.0 (C_5Me_4)	197.5	57.25	118.7, 112.1, 143.9 ($O_2C\mathit{C}_4H_3O$), 158.0 ($O_2\mathit{C}C_4H_3O$)
[{RuCl}CH_2O_2C(2-thienyl)] (**3d**)	9.8, 10.5 (C_5Me_4), 89.4, 100.2, 106.9 (C_5Me_4)	197.5	57.5	128.0, 133.1, 134.0, 132.8 ($O_2CC_4H_3S$); 161.5, ($O_2\mathit{C}C_4H_3S$)
[{RuCl}CHO] (**4a**)	9.6, 10.5 (C_5Me_4), 101.4, 109.7 (C_5Me_4)	195.7	187.8 (CHO)	
[{RuCl}$CHOCH_2CH_2O$] (**5a**)	9.3, 10.3 (C_5Me_4), 88.4, 101.6, 105.5 (C_5Me_4)	197.6	99.5	65.9, ($C_5Me_4CHO_2\mathit{C}H_2\mathit{C}H_2$)
[{RuCl}CHPhOH] (**8a**)	10.2, 10.2, 10.5, 10.8 (C_5Me_4), 96.6, 97.7, 102.7, 105.1, 107.5 (C_5Me_4)	197.7, 198.1	68.5	125.9, 127.7, 128.6, 141.0 ($C_5Me_4CH(OH)\mathit{C}_6H_5$)
[{RuCl}$CH(C_6H_9O)OH$] (**8b**)	9.7, 9.7, 10.7, 11.0 (C_5Me_4), 24.7, 27.7, 30.7, 42.3, (C12, C13, C14, C15), 55.6 (C11), 66.2 (C10), 98.9, 100.8, 100.9, 101.5, 104.4 (C5, C6, C7, C8, C9), 197.8, 197.9 (C17, C18), 212.9 (C16)[b]			
[{RuCl}$CH(CH_2COMe)OH$] (**8c**)	10.0, 10.1, 10.1, 10.6 (C_5Me_4), 97.8, 98.0, 103.1, 104.1, 104.5 (C_5Me_4)	197.7, 197.9	63.3	30.7 ($-CH_2CO\mathit{Me}$), 49.5 ($-\mathit{C}H_2COMe$), 206.8 ($-CH_2\mathit{C}OMe$)
[{RuCl}$CH(CH_2COPh)OH$] (**8d**)	10.0, 10.1, 10.4, 10.8 (C_5Me_4), 97.9, 98.0, 102.6, 104.6, 105.3 (C_5Me_4)	197.8, 198.0	63.7	45.1 ($-\mathit{C}H_2COPh$), 128.3, 128.8, 133.8, 136.4 ($-CH_2CO\mathit{Ph}$), 198.3 ($-CH_2\mathit{C}OPh$)
[{RuCl}$CH{=}CHCO_2Et$] (**9a**)	9.8, 11.3 (C_5Me_4), 89.1, 100.3, 105.9 (C_5Me_4)	197.2	122.5 ($-\mathit{C}H{=}CH-$)	14.2 ($CO_2CH_2\mathit{Me}$), 60.9 ($CO_2\mathit{C}H_2CH_3$), 135.2 ($C_5Me_4CH{=}\mathit{C}HCO_2Et$), 166.1 ($C_5Me_4CH{=}CH\mathit{C}O_2Et$)
[{RuCl}CH=CHPh] (**9b**); *Z* isomer	10.0, 10.75 (C_5Me_4), 99.5, 99.8, 102.7 (C_5Me_4)	198.3	136.2 ($-\mathit{C}H{=}CH-$)	119.4 ($C_5Me_4CH{=}\mathit{C}H\ C_6H_5$), 127.9, 128.2, 128.4, 128.5 ($C_5Me_4CH{=}CH\mathit{C}_6H_5$)
[{RuCl}CH=CHPh] (**9b**); *E* isomer	9.8, 11.1 (C_5Me_4), 97.15, 100.4, 102.1 (C_5Me_4)	198.3	135.1 ($-\mathit{C}H{=}CHPh$)	117.9 ($CH{=}\mathit{C}HPh$), 126.6, 128.2, 128.5, 128.8 ($CH{=}CH\mathit{C}_6H_5$)
[{RuCl}CH=CHCOMe] (**9c**)	10.0, 11.2 (C_5Me_4), 89.6, 100.4, 106.2 (C_5Me_4)	197.3	130.6 ($-\mathit{C}H{=}CH-$)	27.9 ($C_5Me_4CH{=}CHCO\mathit{Me}$), 133.9 ($C_5Me_4CH{=}\mathit{C}HCOMe$), 197.2 ($C_5Me_4CH{=}CH\mathit{C}OMe$)
[{RuCl}CH=CHCOPh] (**9d**)	10.0, 11.3 (C_5Me_4), 89.9, 100.0, 106.6 (C_5Me_4)	197.3	133.2, 134.9 ($-\mathit{C}H{=}\mathit{C}H-$)	126.3, 128.6, 128.8, 137.6 ($C_5Me_4CH{=}CHCO\mathit{C}_6H_5$), 189.5 ($C_5Me_4CH{=}CH\mathit{C}OC_6H_5$)
[{RuCl}CO_2H] (**10**)	9.9, 11.9 (C_5Me_4), 101.2, 110.7 (C_5Me_4),	196.1	171.2 ($-\mathit{C}O_2H$)	
[{RuCl}CON(i-Pr)$_2$] (**12**)	9.5, 11.7 (C_5Me_4) 90.0, 101.5, 106.5 (C_5Me_4),	198.8	168.9 ($\mathit{C}ON(i\text{-}Pr)_2$)	18.9 (Me-i-Pr), 46.3 (CH-i-Pr)

[a] {RuCl} = {(η^5-C_5Me_4−)Ru(CO)$_2$Cl}. [b] Numbering convention for complex **8b**:



magnesium bromide to give [($C_5Me_4CH(OH)Ph$)Ru(CO)$_2$Cl], **8a**, in 76% yield after workup. This complex was characterized by microanalysis and spectroscopically and also by an X-ray crystal structure determination (Figure 1), which confirmed the structure.

Another series of reactions that work for the aldehyde **4a** are those also undergone by organic aromatic aldehydes with lithium enolates of ketones. Thus **4a** reacted with the enolates derived from cyclohexanone, acetone and acetophenone to give the complexes [($C_5Me_4CH(OH)R$)Ru(CO)$_2$Cl] (R = 2-oxocyclohexyl, **8b**; $MeCOCH_2$, **8c**; and $PhCOCH_2$, **8d**) (Scheme 3). Although the yield was only 15% for **8c**, those for **8b**,**d** were much better (41 and 69%, respectively), suggesting that, with optimization, yields can still be significantly improved. In each case the products were identified spectroscopically; the IR spectra showed the ketonic bands at 1699, 1716, and 1682 and ν(OH) at 3612, 3614, and 3686 cm^{-1} respectively for **8b**−**d**. The positions of these last bands suggested the presence of free, not H-bonded, OH.[12] The structure of complex **8d** was confirmed by an X-ray crystal determination (Figure 2), which showed the expected features. The $COCH_2CH(OH)$ unit was quite nonplanar with the two CO bonds roughly perpendicular to each other (dihedral angle between the planes C(8)−C(9)−O(2) and C(8)−C(7)−O(1) is 115°) and with a distance between the two oxygens of 2.88 Å. This suggests that there is no significant H-bonding between the OH and the ketonic C=O of the side chain, a conclusion reinforced by the IR spectra.

We also successfully reacted the aldehyde **4** with a variety of Wittig reagents, $Ph_3P{=}CHR$, derived from their triphenylphosphonium salts $[Ph_3PCH_2R]^+$.[13] These reactions exchanged the =O for =CHR and gave the complexes [($C_5Me_4CH{=}CHR$)Ru(CO)$_2$Cl], **9a**−**d**. The

(12) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 5th ed.; McGraw-Hill: London, 1995; p 41 ff.

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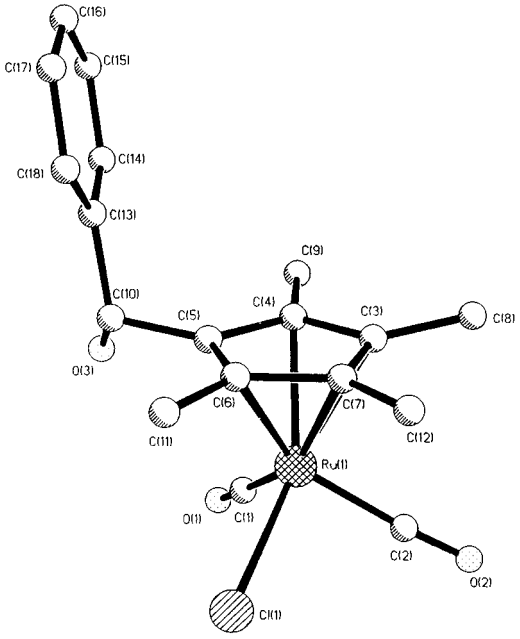
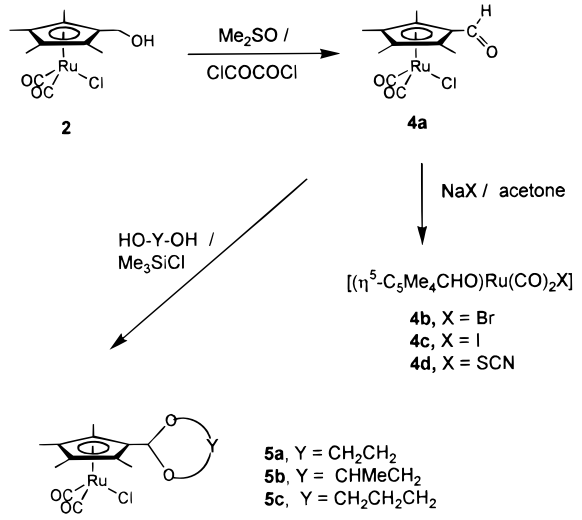


Figure 1. View of the structure of $[(C_5Me_4CHPh(OH))Ru(CO)_2Cl]$, complex **8a**, from the X-ray determination, with hydrogens omitted. Selected bond lengths and angles: Ru(1)−Cl(1) 2.4221(13) Å; Ru(1)−C(1) 1.912(5) Å; Ru(1)−C(2) 1.887(5) Å; Ru(1)−C(3) 2.207(4) Å; Ru(1)−C(4) 2.200(43) Å; Ru(1)−C(5) 2.250(4) Å; Ru(1)−C(6) 2.273(4) Å; Ru(1)−C(7) 2.242(4) Å; C(2)−Ru(1)−C(1) 90.6(2)°; C(2)−Ru(1)−Cl(1), 91.5(2)°; C(1)−Ru(1)−Cl(1), 93.71(14)°.

Scheme 2



best yields were 61% for **9a** (R = CO_2Et) and **9c** (R = COMe), where α,β-unsaturated ene−one functionalities were introduced. In the case of complex **9b**, a substituted styrene, it was possible to isolate and separate the *E* and *Z* isomers, by column chromatography on silica; only the *E*-isomers could be detected for the complexes **9a**,**c**,**d**. The yields of the stereoisomers, 21% of *E*-**9b** and 11% of *Z*-**9b**, respectively, were those actually isolated; they have again not been optimized.

The structures of the complexes were determined by spectroscopic methods, and that of one complex, the

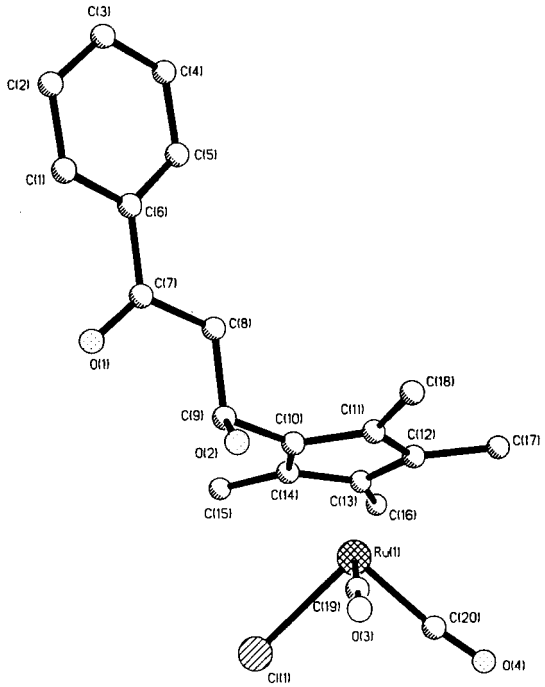
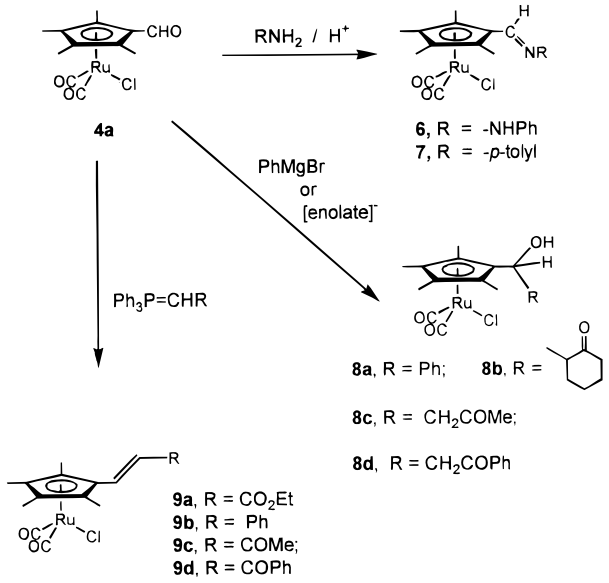


Figure 2. View of the structure of $[(C_5Me_4CH(OH)CH_2COC_6H_5)Ru(CO)_2Cl]$, complex **8d**, from the X-ray determination, with hydrogens omitted. Selected bond lengths and angles: Ru(1)−Cl(1) 2.431(2) Å; Ru(1)−C(19) 1.902(6) Å; Ru(1)−C(20) 1.877(9) Å; Ru(1)−C(10) 2.225(4) Å; Ru(1)−C(11) 2.215(5) Å; Ru(1)−C(12) 2.221(5) Å; Ru(1)−C(13) 2.253(5) Å; Ru(1)−C(14) 2.275(5) Å; C(20)−Ru(1)−C(19) 90.5(3)°; C(20)−Ru(1)−Cl(1), 92.9(4)°; C(19)−Ru(1)−Cl(1), 90.4(2)°.

Scheme 3



styryl *E*-**9b**, was confirmed by an X-ray structure determination (Figure 3).

Carboxylic Acid Complex 10 and Complexes 11 and 12 Derived from It. A further most surprising reaction was the oxidation, by potassium permanganate in aqueous acetone at 40 °C, of the aldehyde **4a** to give the carboxylic acid, $[(C_5Me_4CO_2H)Ru(CO)_2Cl]$, **10,** in 64% isolated yield. Under the conditions specified there appeared to be no oxidation of the metal. The free acid exhibited ν(CO) at 1732 cm^{-1} in CH_2Cl_2 solution sug-

(13) Hudson, C. M.; Marzabadi, M. R.; Moeller, K. D.; New, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 7372.

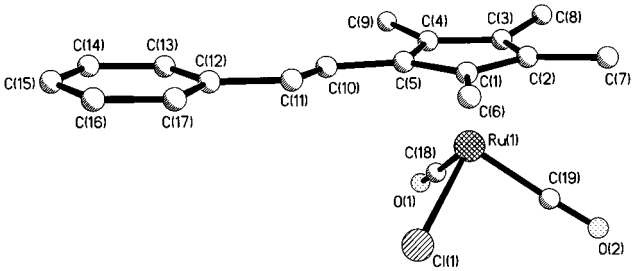
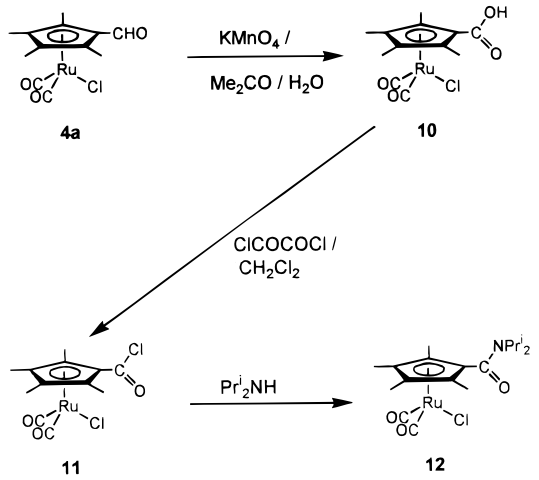


Figure 3. View of the structure of [(C_5Me_4CH═$CHPh$)-$Ru(CO)_2Cl$], complex **9b**, from the X-ray determination, with hydrogens omitted. Selected bond lengths and angles: Ru(1)−Cl(1) 2.4132(13) Å; Ru(1)−C(1) 2.259(3) Å; Ru(1)−C(2) 2.246(3) Å; Ru(1)−C(3) 2.203(4) Å; Ru(1)−C(4) 2.239(3) Å; Ru(1)−C(5) 2.256(3) Å; Ru(1)−C(18) 1.900(5) Å; Ru(1)−C(19) 1.888(4) Å; C(19)−Ru(1)−C(18) 90.3(2)°; C(19)−Ru(1)−Cl(1), 89.3(2)°; C(18)−Ru(1)−Cl(1), 94.41-(14)°.

Scheme 4



gesting that it was present as the monomeric un-ionized and unpolarized −C═O(OH).[12] Scheme 4 shows the formation of the acid and its further reactions. The acid was converted into the acid chloride [(C_5Me_4COCl)Ru-$(CO)_2Cl$], **11**, a highly reactive and unstable species, by reaction with oxalyl chloride in CH_2Cl_2. The acid chloride **11** reacted with diisopropylamine in situ in the presence of triethylamine to give the amide [(C_5Me_4CON-(i-Pr)$_2$)$Ru(CO)_2Cl$], **12**, in 59% overall yield from **10**.

Although the actual molecule is quite different, we have found somewhat related structures for some (permethylcyclopentadienyl)iridium complexes.[14] Here the parent complex [{(η^5-C_5Me_5)Ir(Ph)(Me)(CO)] was activated at the ring methyl C−H by reaction with strong nucleophiles (*sec*-BuLi) to give Li[{(η^5-$C_5Me_4CH_2$)Ir(Ph)-(Me)(CO)] which reacted further with electrophilic reagents, for example carbon dioxide, to give the carboxylic acid, [{(η^5-$C_5Me_4CH_2CO_2H$)Ir(Ph)(Me)(CO)], ν-(CO_2) at 1707 cm^{-1}.

NMR Spectra of the New Complexes. The ^1H and ^{13}C NMR spectra (Tables 2 and 3) allow the characterization of the molecules; in particular the number of C_5-Me_4 resonances seen reflect the symmetry of the molecule. Thus all the complexes **3**−**7**, **9**, **10**, and **12** show the methyls as two singlets in a 1:1 ratio, reflecting the equivalence of the two types of methyls and consistent with the presence of a plane of symmetry perpendicular to the plane of the ring and passing through the C_5−CH and the Ru−Cl bonds. On the other hand, the spectra of complexes **8a**−**d**, where the methyls are diastereotopic by virtue of the chiral center at −CH(OH)R, show four separate methyls. The other substituents are also clearly identified in the spectra.

X-ray Structures of Complexes 8a,d and 9b. As mentioned in the appropriate sections above, the structures of complexes [($C_5Me_4CHPh(OH)$)$Ru(CO)_2Cl$], **8a**, [($C_5Me_4CH(OH)CH_2COPh$)$Ru(CO)_2Cl$], **8d**, and [(C_5Me_4-CH═CHPh)$Ru(CO)_2Cl$], **9b**, have been confirmed by X-ray determinations. In each case the molecule comprises a piano-stool arrangement of the η^5-C_5Me_4R ligand with the three legs represented by the two CO's and the Cl on the other side. These three ligands are arranged octahedrally, the three angles between them being very close to 90°. In each case the Ru−Cl distance was close to 2.42 Å; that of the Ru−CO averaged 1.894 Å, while the Ru to carbon distances in the η^5-C_5Me_4R ring were also very similar, in the range 2.20−2.27 Å. The R substituent was on the carbon most nearly trans to one of the CO ligands, and the solid-state arrangement favored the side chain R being away from the metal. The near planar PhCH═CHC_5Me_4 and the *E*-arrangement of the double bond in **9b** as well as the nonplanar $CH(OH)CH_2COPh$ in **8d** were also clearly seen.

Conclusion

We have described a wide variety of organic transformations which take place at the ring CH_2Cl of [($C_5Me_4CH_2Cl$)$Ru(CO)_2Cl$], complex **1**, with remarkable facility and without significantly affecting the Ru-$(CO)_2Cl$. They include hydrolysis to the alcohol, which is then oxidized to the aldehyde and then to the carboxylic acid. Each of these undergoes organic reactions typical of the functionality present: The alcohol gives esters, and the aldehyde forms acetals, undergoes aldol condensations with enolates, and reacts with Grignard and with Wittig reagents, while the carboxylic acid forms amides. These reactions occur without significantly affecting the $Ru(CO)_2Cl$, but this can be modified in subsequent steps, allowing access to a wide variety of new types of functionalized (permethylcyclopentadienyl)ruthenium complexes. New complexes have been characterized spectroscopically and with the help of three X-ray structure determinations.

Experimental Section

Reactions were carried out using standard Schlenk line techniques; solvents and reagents were purified and dried by standard methods. Microanalyses (Table 1) were performed by the Sheffield University Microanalysis Service. IR spectra (Table 1) were recorded in dichloromethane solution on a Perkin-Elmer PE1600 FTIR spectrometer. ^1H and ^{13}C NMR spectra (Tables 2 and 3) were recorded on Bruker AM250 or AC250 instruments using the solvent or tetramethylsilane as internal standard.

Preparation of [($C_5Me_4CH_2OH$)$Ru(CO)_2Cl$] (2). [(C_5Me_4-CH_2Cl)$Ru(CO)_2Cl$] (**1**, 1.14 g, 3.1 mmol) was dissolved in THF (40 mL) together with water (5 mL) and collidine (0.42 mL, 3.2 mmol) and refluxed (2 h). Excess solvent was removed,

(14) Miguel-Garcia, J. A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1992**, 131.

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and the residue extracted with ether; the ether extract was concentrated and chromatographed (silica column/ether). The second yellow band was collected and excess solvent removed to give bright yellow [($C_5Me_4CH_2OH$)Ru(CO)$_2$Cl], 0.87 g, 92%: IR ν(CO) 2038, 1986 cm^{-1}.

Reaction of [($C_5Me_4CH_2OH$)Ru(CO)$_2$Cl] (2) with CH_3COCl To Make [($C_5Me_4CH_2O_2CMe$)Ru(CO)$_2$Cl] (3a). [($C_5Me_4CH_2OH$)Ru(CO)$_2$Cl] (0.07 g, 0.2 mmol) was dissolved in dry dichloromethane (10 mL) together with Et_3N (0.045 mL, 0.33 mmol). Acetyl chloride (0.018 mL, 0.2 mmol) was then added and the solution stirred under nitrogen for 0.5 h. Excess solvent was removed and the residue extracted with ether. The ether extract was concentrated and chromatographed on a silica column in ether. The first band was collected and the solvent removed to give [($C_5Me_4CH_2O_2CMe$)Ru(CO)$_2$Cl] as a yellow solid, yield 0.05 g, 65%.

[($C_5Me_4CH_2O_2CCH{=}CH_2$)Ru(CO)$_2$Cl] (3b) was prepared in the same manner as **3a**, from [($C_5Me_4CH_2OH$)Ru(CO)$_2$Cl] (**2**, 0.063 g, 0.18 mmol) and acryloyl chloride (0.019 mL, 0.24 mmol); yield 0.047 g, 65%.

[($C_5Me_4CH_2O_2CC_4H_3O$)Ru(CO)$_2$Cl] (3c) was prepared as **3a** above, from [($C_5Me_4CH_2OH$)Ru(CO)$_2$Cl] (0.13 g, 0.39 mmol) and 2-furoyl chloride (0.06 mL, 0.59 mmol); yield 0.115 g, 68%.

[($C_5Me_4CH_2O_2CC_4H_3S$)Ru(CO)$_2$Cl] (3d) was prepared as **3a** above, from [($C_5Me_4CH_2OH$)Ru(CO)$_2$Cl] (0.15 g, 0.44 mmol) and thiophene-2-carbonyl chloride (0.07 mL, 0.66 mmol); yield 0.133 g, 67%.

Preparation of [(C_5Me_4CHO)Ru(CO)$_2$Cl] (4a) Using Oxalyl Chloride and Me_2SO. Oxalyl chloride (1.39 mL, 2.8 mmol; 2 M solution in dichloromethane) was dissolved in dry dichloromethane (10 mL) under nitrogen, in a three necked round-bottomed flask equipped with two pressure-equalizing addition funnels. One funnel contained Me_2SO (0.45 mL, 6.3 mmol) dissolved in dichloromethane (3 mL), and the other contained [($C_5Me_4CH_2OH$)Ru(CO)$_2$Cl] (**2**, 0.87 g, 2.5 mmol) dissolved in dichloromethane (5 mL). The contents of the flask were cooled (−60 °C), and the Me_2SO solution was added dropwise. Stirring was continued (−60 °C, 15 min), and then the alcohol solution was added dropwise; the reaction mixture was stirred (−60 °C, 20 min), and Et_3N (1.75 mL, 12.7 mmol) was added and then slowly allowed to warm to +20 °C, when water (15 mL) was added. The organic layer was separated, dried ($MgSO_4$), concentrated, and chromatographed (silica/dichloromethane). The first yellow band was collected to give [(C_5Me_4CHO)Ru(CO)$_2$Cl], **4a**, as a bright yellow solid, 0.71 g, 82%.

Preparation of [(C_5Me_4CHO)Ru(CO)$_2$I] (4c). Sodium iodide (0.02 g, 0.15 mmol) was added to [(C_5Me_4CHO)Ru(CO)$_2$Cl], **4a** (0.05 g, 0.15 mmol), dissolved in acetone (15 mL) and the solution refluxed (17 h). The acetone was then removed in vacuo, the residue was extracted with dichloromethane, washed with water, and dried, and the solvent was again removed to yield a solid which crystallized from diethyl ether/pentane as orange-yellow crystals of the iodide, **4c** (0.054 g, 85%). The bromide and thiocyanate were made similarly.

[($C_5Me_4CH(OCH_2)_2$)Ru(CO)$_2$Cl] (5a) from [(C_5Me_4CHO)Ru(CO)$_2$Cl] (4a) and Ethylene Glycol. [(C_5Me_4CHO)Ru(CO)$_2$Cl], **4a** (0.15 g, 0.44 mmol), dissolved in dry dichloromethane (10 mL) together with ethylene glycol (0.05 mL, 0.9 mmol) and trimethylchlorosilane (0.25 mL, 2.0 mmol), was refluxed (24 h). An aqueous solution of sodium hydrogen carbonate (5%, 20 mL) was then added and the product extracted into dichloromethane; after workup the solvent was removed, and the product [($C_5Me_4CH(OCH_2)_2$)Ru(CO)$_2$Cl], **5a** (0.13 g, 74%), was obtained (dichloromethane−pentane) as yellow crystals.

Preparation of [($C_5Me_4CH{=}NNHPh$)Ru(CO)$_2$Cl] (6). [(C_5Me_4CHO)Ru(CO)$_2$Cl], **4a** (0.1 g, 0.29 mmol), was added to phenylhydrazine (0.03 mL, 0.3 mmol) in a warm mixture of ethanol (3.5 mL) and hydrochloric acid (concentrated, 0.4 mL) and the solution heated. On cooling, the solution gave an orange crystalline precipitate of the phenylhydrazone, **6** (0.096 g, 91%).

Preparation of [($C_5Me_4CH{=}N$-*p*-To)Ru(CO)$_2$Cl] (7). *p*-Toluenesulfonic acid (2.5 mg) was added to a solution of [(C_5Me_4CHO)Ru(CO)$_2$Cl], **4a** (0.1 g, 0.29 mmol), and *p*-toluidine (0.032 g, 0.29 mmol), dissolved in chloroform (20 mL) and the solution refluxed (3 h). The solution was cooled and filtered and the solvent removed; the residue was chromatographed on a silica column in diethyl ether−light petroleum (80:20) to give a yellow band which yielded **7** as a yellow solid (0.07 g, 58%).

[($C_5Me_4CHPh(OH)$)Ru(CO)$_2$Cl] (8a) from [(C_5Me_4CHO)Ru(CO)$_2$Cl] (4a) and PhMgBr. A solution of PhMgBr in diethyl ether (0.1 mL, 3 M solution, 0.3 mmol, Aldrich) was added dropwise to [(C_5Me_4CHO)Ru(CO)$_2$Cl] (**4a**, 0.1 g, 0.29 mmol) in dry THF (5 mL; −78 °C) and the solution stirred (−78 °C, 2.5 h). The reaction was then quenched with dilute HCl (25 mL), stirred (10 min), and extracted with ether, and the ether extract was dried ($MgSO_4$) and chromatographed (silica/dichloromethane). The first yellow band was collected and solvent removed to give a yellow oil, which was crystallized (ether−pentane) giving bright yellow crystals of [($C_5Me_4CHPhOH$)Ru(CO)$_2$Cl], 0.14 g, 76%.

[($C_5Me_4CH(OH)C_6H_9O$)Ru(CO)$_2$Cl] (8b) from [(C_5Me_4CHO)Ru(CO)$_2$Cl] (4a) and Li[C_6H_9O]. BuLi (0.190 mL, 2.6 M solution in hexane, 0.48 mmol, Aldrich) was added to diisopropylamine (0.064 mL, 0.48 mmol) dissolved in THF (4 mL; 0 °C). The solution was then cooled (−78 °C), cyclohexanone (0.045 mL, 0.44 mmol) added, and the solution stirred (−78 °C, 1 h). [(C_5Me_4CHO)Ru(CO)$_2$Cl] (0.15 g, 0.44 mmol) in THF (5 mL) was then added and the solution stirred (1 h, −78 °C); the reaction was then quenched (ammonium chloride solution) and allowed to warm (+20 °C), and the organic layer was dried ($MgSO_4$), concentrated, and chromatographed (silica−dichloromethane). The first yellow band was collected to give a yellow oil, which was crystallized (dichloromethane−pentane) giving yellow crystals of [($C_5Me_4CH(OH)C_6H_9O$)Ru(CO)$_2$Cl], **8b,** yield 0.079 g, 41%.

[($C_5Me_4CH(OH)CH_2COMe$)Ru(CO)$_2$Cl] (8c) from [(C_5Me_4CHO)Ru(CO)$_2$Cl] and Li[CH_2COMe]. The lithium enolate of acetone was made by reaction of lithium diisopropylamide (from BuLi, 0.19 mL, 2.5 M solution, 0.48 mmol) and acetone (0.03 mL, HPLC grade, 0.4 mmol) in THF at −78 °C; to this was added [(C_5Me_4CHO)Ru(CO)$_2$Cl] (0.15 g, 0.44 mmol) in THF (4 mL). After workup as above, a yellow oil was obtained, which was chromatographed (silica−diethyl ether) to give a first yellow band which gave an oil, that crystallized from ether (plus one drop of ethanol) and pentane to give [($C_5Me_4CH(OH)CH_2COMe$)Ru(CO)$_2$Cl], **8c**, 0.0265 g, 15%.

[($C_5Me_4CH(OH)CH_2COC_6H_5$)Ru(CO)$_2$Cl] (8d) from [($C_5Me_4CHO$)Ru(CO)$_2$Cl] and Li[$CH_2COC_6H_5$]. This was carried out in the same way as above, reacting lithium diisopropylamide, (0.48 mmol), acetophenone (0.054 mL, 0.46 mmol), and [(C_5Me_4CHO)Ru(CO)$_2$Cl] (0.15 g, 0.44 mmol). Workup gave [($C_5Me_4CH(OH)CH_2COC_6H_5$)Ru(CO)$_2$Cl], **8d,** as yellow crystals, 0.018 g, 9%.

[($C_5Me_4CH{=}CHCO_2Et$)Ru(CO)$_2$Cl] (9a) from [(C_5Me_4CHO)Ru(CO)$_2$Cl] and (Ethylacetylidene)triphenylphosphorane. Na[$MeSOCH_2$], from NaH (0.04 g, 1 mmol, washed with hexane) and Me_2SO (3 mL), was added to a solution of ethyl (triphenylphosphonio)acetate bromide (0.4 g, 0.9 mmol, from ethyl bromoacetate and triphenylphosphine) in Me_2SO (5 mL). The solution was stirred (45 min); then a solution of [(C_5Me_4CHO)Ru(CO)$_2$Cl] (0.15 g, 0.4 mmol) in Me_2SO (5 mL) was added. The resulting solution was stirred (1 h) and then quenched (diethyl ether and water); the ether extract was dried ($MgSO_4$) and chromatographed (silica−dichloromethane). The second yellow band was collected and solvent removed to give

a yellow oil, which was crystallized (dichloromethane−hexane) giving yellow crystals of [($C_5Me_4CH{=}CHCO_2Et$)$Ru(CO)_2Cl$], **9a,** yield, 60%.

[($C_5Me_4CH{=}CHPh$)$Ru(CO)_2Cl$] (9b) from [(C_5Me_4CHO)$Ru(CO)_2Cl$] and Benzylidenetriphenylphosphorane. Na[$MeSOCH_2$], made from NaH (0.05 g, 1.3 mmol, washed with hexane) and Me_2SO (3 mL), was added to a solution of benzyltriphenylphosphonium bromide (0.51 g, 1.2 mmol) in Me_2SO (5 mL). After the mixture was stirred (30 min) a solution of [(C_5Me_4CHO)$Ru(CO)_2Cl$] (0.2 g, 0.6 mmol) in Me_2SO (5 mL) was added, and the resulting solution stirred (2 h). The reaction was then quenched with ether and water and worked up as above; chromatography (silica−dichloromethane) gave a yellow band which yielded a bright yellow oil that crystallized. ^1H NMR of the solid showed that it was a mixture of *E* and *Z* isomers of [($C_5Me_4CH{=}CHPh$)$Ru(CO)_2Cl$], **9b**, ratio 6:5, which were separated by preadsorption onto a silica column and eluting with ethyl acetate−petroleum ether, bp 40−60 °C. The first yellow band, 0.028 g, 11% isolated yield, was the *Z* isomer, while the second yellow band, 0.051 g, 21%, was the *E* isomer, both identified spectroscopically.

[($C_5Me_4CH{=}CHCOMe$)$Ru(CO)_2Cl$] (9c) from [(C_5Me_4CHO)$Ru(CO)_2Cl$] and Acetonylidenetriphenylphosphorane. This was made by reaction of the Wittig reagent $MeCOCHPPh_3$ (from acetonyltriphenylphosphonium chloride, 0.31 g, 0.88 mmol) in Me_2SO (5 mL) and [(C_5Me_4CHO)$Ru(CO)_2Cl$] (0.15 g, 0.44 mmol) in Me_2SO (5 mL) at 50 °C (2 h). After workup the product was obtained as yellow crystals, 0.10 g, 61%.

[($C_5Me_4CH{=}CHCOPh$)$Ru(CO)_2Cl$] (9d) from [(C_5Me_4CHO)$Ru(CO)_2Cl$] and (2-Acetophenylidene)triphenylphosphorane. This was made by reaction of the Wittig reagent $PhCOCHPPh_3$ (from triphenylphosphonium acetophenone bromide, 0.41 g, 0.88 mmol) in Me_2SO (5 mL) and [(C_5Me_4CHO)$Ru(CO)_2Cl$] (0.15 g, 0.44 mmol) in Me_2SO (5 mL) at 50 °C (2 h). After workup the *E* isomer, **9d,** 0.057 g, 13%, was isolated by column chromatography.

Oxidation of [(C_5Me_4CHO)$Ru(CO)_2Cl$] to [($C_5Me_4CO_2H$)$Ru(CO)_2Cl$] (10) with $KMnO_4$. A hot solution of $KMnO_4$ (0.18 g, 1.1 mmol) in water (2 mL) − acetone (10 mL) was added dropwise to [(C_5Me_4CHO)$Ru(CO)_2Cl$], **4a** (0.2 g, 0.59 mmol), dissolved in acetone (5 mL); the solution was stirred (40 °C, 50 min) and filtered to give a yellow solution. Excess acetone was removed in vacuo and water (5 mL) added; the aqueous solution was then made basic (∼pH 10) with 5% aqueous $NaHCO_3$ and extracted with dichloromethane; the extracts were discarded. The aqueous solution was then made acidic with dilute HCl and extracted with dichloromethane; after drying ($MgSO_4$), the solvent was removed to give pale orange/brown [($C_5Me_4CO_2H$)$Ru(CO)_2Cl$], **10**, 0.13 g, 64%.

Preparation of [(C_5Me_4COCl)$Ru(CO)_2Cl$] (11) and [($C_5Me_4CON(i\text{-}Pr)_2$)$Ru(CO)_2Cl$] (12). [($C_5Me_4CO_2H$)$Ru(CO)_2Cl$] (0.134 g, 0.38 mmol) was dissolved in dry dichloromethane (10 mL) together with oxalyl chloride (0.188 mL, 2 M soliton in CH_2Cl_2, 0.38 mmol) and the solution stirred (18 h). Excess solvent was then removed under high vacuum to give [(C_5Me_4COCl)$Ru(CO)_2Cl$], **11**. This acid chloride was not isolated but was dissolved in dry dichloromethane (8 mL), and a solution of diisopropylamine (0.1 mL, 0.76 mmol) and Et_3N (0.05 mL, 0.36 mmol) in dry dichloromethane (4 mL) was added dropwise. The solution was stirred (6 h), excess solvent was removed, and the product was crystallized from ethanol and pentane, giving bright yellow crystals of [(C_5Me_4CON-(i-Pr)$_2$)$Ru(CO)_2Cl$], **12**, 0.099 g, 59%.

X-ray Structure Determinations of Complexes (8a,d and 9b). Crystal Data for Complex 8a: $C_{18}H_{19}ClO_3Ru$, M_r = 419.85, crystallized from ether−pentane as yellow blocks; crystal dimensions 0.72 × 0.43 × 0.29 mm; triclinic; a = 8.909(2), b = 9.135(2), c = 12.145(3) Å; α = 109.16(2), β = 99.39(3), γ = 101.14(2)°; V = 888.3(4) Å^3; Z = 2; D_c = 1.570 Mg/m^3; space group $P\bar{1}$ (C_i^1, No. 2); Mo Kα radiation ($\bar{\lambda}$ = 0.710 73 Å), μ(Mo Kα) = 1.043 mm^{-1}, F(000) = 424.

Three-dimensional, room-temperature X-ray data were collected in the range 3.5 < 2θ < 45° on a Siemens P4 diffractometer by the ω scan method. Of the 2801 reflections measured, all of which were corrected for Lorentz and polarization effects (but not for absorption), 2125 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0309 (wR_2 = 0.0858 for all 2270 unique data, 208 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. The minimum and maximum final electron densities were −0.495 and 0.410 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.6166P]$, where $P = (F_o^2 + 2Fc_2)/3$, was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[15] as implemented on the Viglen 486dx computer.

Crystal Data for Complex 8d: $C_{20}H_{21}ClO_4Ru$, M_r = 461.89, crystallized from ether−pentane as yellow blocks; crystal dimensions 0.72 × 0.44 × 0.34 mm; triclinic; a = 8.042(2), b = 9.279(2), c = 14.800(3) Å; α = 103.87(3), β = 98.72(3), γ = 104.08(3)°; V = 1013.8(4) Å^3; Z = 2; D_c = 1.513 Mg/m^3; space group $P\bar{1}$ (C_i^1, No. 2); Mo Kα radiation ($\bar{\lambda}$ = 0.710 73 Å), μ(Mo Kα) = 0.925 mm^{-1}, F(000) = 468.

Three-dimensional, room-temperature X-ray data were collected in the range 3.5 < 2θ < 50° on a Siemens P4 diffractometer by the ω scan method. Of the 4362 reflections measured, all of which were corrected for Lorentz and polarization effects (but not for absorption), 3134 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in the riding mode. Refinement converged at a final R = 0.0504 (wR_2 = 0.1391 for all 3540 unique data, 237 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. The minimum and maximum final electron densities were −1.035 and 0.782 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0931P)^2 + 1.7660P]$, where $P = (F_o^2 + 2F_c^2)/3$, was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[14] as implemented on the Viglen 486dx computer.

Crystal Data for Complex 9b: $C_{19}H_{19}Cl_2O_2Ru$, M_r = 415.86, crystallized from dichloromethane−pentane as yellow blocks; crystal dimensions 0.360 × 0.195 × 0.125 mm; monoclinic; a = 13.590(2), b = 8.237(3), c = 17.377(2) Å; β = 110.500(10)°; V = 1821.4(7) Å^3; Z = 4; D_c = 1.517 Mg/m^3, space group $P2_1/n$ (a nonstandard setting of $P2_1/c$, C_{2h}^5, No. 14); Mo Kα radiation ($\bar{\lambda}$ = 0.710 73 Å), μ(Mo Kα) = 1.013 mm^{-1}, F(000) = 840.

Three-dimensional, room-temperature X-ray data were collected in the range 3.5 < 2θ < 50° on a Siemens P4 diffractometer by the ω scan method. Of the 4099 reflections measured, all of which were corrected for Lorentz and polarization effects (but not for absorption), 2678 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$ The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0350 (wR_2 = 0.095, for all 3198 unique data 208 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy

(15) Sheldrick, G. M. *SHELXL93: An Integrated System for Solving and Refining Crystal Structures from Diffraction Data*; University of Gottingen, Gottingen, Germany, 1993.

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of all non-hydrogen atoms. The minimum and maximum final electron densities were −0.950 and 0.340 e A^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.0608P]$, where $P = (F_o^2 + 2F_c^2)/3$, was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[14] as implemented on the Viglen 486dx computer.

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Supporting Information Available: Tables of crystal data, anisotropic thermal vibrational parameters with esds, complete atom positional and *U* parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

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