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Preliminary communication

Promotion of acetophenone formation from methyl(phenyl)rhodium carbonyl complexes by organic halides

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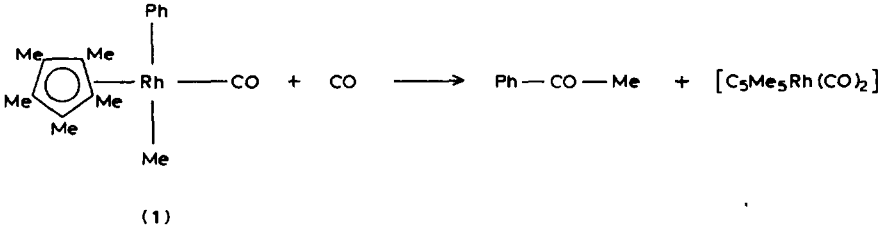
Abstract

[$C_5Me_5RhPh(CO)CH_3$] reacted thermally to give acetophenone (27%) and toluene (9%); acetophenone formation was substantially increased in the presence of halobenzenes PhX (the order of effectiveness being X = I > Br > Cl) or methyl iodide, but 1-electron oxidisers promoted C–C coupling (toluene formation).

Ketones can be formed by the coupling of two organic fragments and CO on a metal [1–8] but good catalytic syntheses are still rare [9–11]. The interest in this area prompts us to communicate studies on the formation of acetophenone by coupling Me, CO, and phenyl in complex **1** [12], where the mutual *cis*-orientation of the three combining groups simplifies the stereochemical requirements of the reaction.

The transformation of **1** into acetophenone occurred readily on carbonylation in acetonitrile (99% yield after 20 h/20 °C/30 atm) but less easily in cyclohexane (only 32% after 166 h/20 °C/5 atm; 99% after 6 h/100 °C/7.5 atm); the other product was [$C_5Me_5Rh(CO)_2$].



Under nitrogen **1** decomposed only slowly on heating, to give PhCOMe (27%) and toluene (9%); some methane was also produced (Table 1). However, acetophenone formation was substantially promoted by organic halides; toluene formation remained little affected. Thus, when complex **1** was treated with 2.4 equivalents of halobenzene in cyclohexane, the order of effectiveness found was

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Table 1

Products from decomposition of $[C_5Me_5Rh(Me)CO(Ph)]$ (1)

Conditions	T (°C)/h	PhCOMe (μmol)	PhMe (μmol)	other organics (μmol)	metal complex
[a]	100/6	27	9	CH_4 19	[b]
[a] + PhI (240 μmol)	100/6	70	12	CH_4 tr Ph–Ph 80	$[(C_5Me_5RhI_2)_2]$
[a] + PhBr (240 μmol)	100/6	54	8	CH_4 16	$[(C_5Me_5RhBr_2)_2]$
[a] + PhCl (240 μmol)	100/6	34	7	CH_4 21	[c]
PhI [d]	100/2	93	6	Ph–Ph 95 CH_4 tr	$[(C_5Me_5RhI_2)_2]$
PhBr [d]	100/2	90	7	Ph–Ph 25 CH_4 5	$[(C_5Me_5RhBr_2)_2]$
PhCl [d]	100/2	80	5	Ph–Ph 1 CH_4 18	[c]
[a] + MeI (450 μmol)	100/6	87	11	CH_4 48 C_2H_4 3 C_2H_6 8	$[(C_5Me_5RhI_2)_2]$
Na_2IrCl_6 [e]	70/1	tr	(96%) [f]	CH_4 tr	
$FeCl_3$ [g]	50/3.5	tr	(91%) [h]	CO (not estd.) CH_4 tr	
CO [j]	20/166	(32%)	[k]		$[C_5Me_5Rh(CO)_2]$
CO [l]	100/6	99	<1		$[C_5Me_5Rh(CO)_2]$

[a] Complex **1** (100 μmol) in cyclohexane (0.5 cm^3; sealed tube). [b] Organometallic residue is a mixture containing carbonyl complexes: ν(CO) typically 1746, 1778 (1791), 1818, 1944, and 1965 cm^{-1}. [c] PhCl recovered essentially in full at the end of the reaction. [d] Complex **1** (100 μmol) in halobenzene (0.5 cm^3; sealed tube). [e] Complex **1** (50 μmol) plus $Na_2IrCl_6 \cdot 6H_2O$ (160 μmol) in moist cyclohexane (2 cm^3), sealed flask. [f] Yield 48 mmol toluene. [g] Complex **1** (50 μmol) plus $FeCl_3$hydrate (160 μmol) in moist cyclohexane (2 cm^3), sealed flask. [h] Yield 45.4 μmol toluene; at 20 °C/24 h this reaction gave 39 μmol toluene (78%). [j] Complex **1** (50 μmol) in cyclohexane (2 cm^3) plus CO (5 atm) in a thick-walled glass tube; 166 h/20 °C. [k] None detected. [l] Complex **1** (100 μmol) in cyclohexane (4 cm^3) plus CO (7.5 atm) in a thick-walled glass tube; 6 h/100 °C.

PhI > PhBr > PhCl, the last showing little improvement over the reaction in neat cyclohexane.

A major product from the reaction in iodobenzene, formed in amount equal to acetophenone, was biphenyl. The organometallic product was $[(C_5Me_5RhI_2)_2]$; we interpret these data to indicate that the major ($\geq$ 70%) reaction pathway is:

$$2\left[C_5Me_5RhMe(CO)Ph\right] + 4PhI \rightarrow 2MeCOPh + 2Ph\text{–}Ph + \left[(C_5Me_5RhI_2)_2\right]$$

The analogous reaction in the presence of bromobenzene gave $[(C_5Me_5RhBr_2)_2]$; much less biphenyl than in the reaction with iodobenzene was formed there.

More marked enhancements occurred in reactions in the neat halobenzene as solvent; again, biphenyl formation decreased in the order PhI > PhBr ≫ PhCl.

Acceleration of acetophenone formation also occurred with methyl iodide. Further, the PhCOMe obtained from reaction of all-protio-**1** in CD_3I as solvent contained no significant deuterium, but the gases formed (mainly methane, but some ethene and ethane) were largely (ca. 80–85%) deuteriated.

We suggest that organic iodides significantly improve C–C–C coupling (ketone formation) while having little effect on C–C coupling (toluene formation), because they facilitate migration onto coordinated CO *, prior to a reductive elimination of PhCOMe. Oxidative addition of RI and coupling to give R–R presumably takes place subsequently. If it occurred earlier, then the reaction of **1** with CD_3I should have also given some CD_3COPh, which was not observed:

$$[C_5Me_5RhMe(CO)Ph] + I\text{–}R \rightarrow [C_5Me_5RhMe(COPh) \cdot (I\text{–}R)]$$
$$\rightarrow PhCOMe + [C_5Me_5RhR(I)]$$
$$[C_5Me_5RhR(I)] + RI \rightarrow \tfrac{1}{2}[(C_5Me_5RhI_2)_2] + R\text{–}R$$

The order of effectiveness, PhI > PhBr > PhCl, parallels the expected nucleophilicity of the halides towards Rh. Such promotion by organic halides acting as Lewis bases does not appear to have previously been noted, but ionic iodide has been shown to promote migration in $[MeMn(CO)_5]$ [13]. This provides an interesting contrast to the observation that Lewis acids promote migration on to coordinated CO [14].

By contrast, one-electron oxidants (e.g. Na_2IrCl_6 or $FeCl_3$hydrate), which have promoted other C–C–C couplings [15], only caused C–C coupling in **1** to give toluene (90–95%). CO was evolved from the system, and none was incorporated. We presume that oxidation at the metal centre in **1** facilitated release of CO and C–C coupling and that migration on to coordinated CO was too slow to compete effectively.

The C–C coupling is also favoured by electron-withdrawing substituents on the aryl. Thus, the major products from the thermal decomposition (hexadeuteriobenzene, 80 °C, 48 h) of $[C_5Me_5RhMe(CO)(p\text{-}C_6H_4CN)]$ were $p\text{-}NCC_6H_4Me$ (48%) and benzonitrile (32%); only a small amount of *p*-acetylbenzonitrile (11%) was formed. In this case the organometallic product was the deep blue dinuclear $[\{C_5Me_5Rh(CO)\}_2]$, $\nu(CO)$ 1733 cm^{-1}, [16] formed according to:

$$2[C_5Me_5RhMe(CO)(p\text{-}C_6H_4CN)] \rightarrow [\{C_5Me_5Rh(CO)\}_2] + 2p\text{-}NCC_6H_4Me$$

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References

1 T. Yamamoto, T. Kohara, and A. Yamamoto, Bull. Chem. Soc., Japan, 54 (1981) 2161.
2 D.R. Saunders and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1984) 2133.
3 N.E. Schore, C.S. Ilenda, M.A. White, H.E. Bryndza, M.G. Matturo, and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 7451.
4 G. Tanguy, B. Weinberger and H. des Abbayes, Tetrahedron Lett., 25 (1984) 5529; P. Laurent, G. Tanguy and H. des Abbayes, J. Chem. Soc., Chem. Commun., (1986) 1754.
5 G. Sundararajan and J. San Filippo, Organometallics, 4 (1985) 606.
6 K.H. Whitmire, T.R. Lee and E.S. Lewis, Organometallics, 5 (1986) 987.
7 B. Hessen, J.H. Teuben, T.H. Lemmen, J.C. Huffman and K.G. Caulton, Organometallics, 4 (1985) 946.

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* Other work suggests that phenyl migrates faster than methyl in these systems.

8 Y. Hayashi, T. Yamamoto, A. Yamamoto, S. Komiya and Y. Kushi, J. Am. Chem. Soc., 108 (1986) 385.
9 K. Murata and A. Matsuda, Bull. Chem. Soc. Japan, 54 (1981) 249; 2089.
10 M. Miura, F. Akase and M. Nomura, J. Chem. Soc., Chem. Commun., (1986) 241.
11 A.R. Dodds and T. Imai, US Patent 4,299,989, 1981; Chem. Abstr., 96 (1982) P85060z.
12 M. Gomez, J.M. Kisenyi, G.J. Sunley and P.M. Maitlis, J. Organomet. Chem., 296 (1985) 197.
13 F. Calderazzo and K. Noack, J. Organomet. Chem., 4 (1965) 250; Coord. Chem. Rev., 1 (1966) 118.
14 T.G. Richmond, F. Basolo, and D.F. Shriver, Inorg. Chem., 21 (1982) 1272.
15 I.M. Saez, N.J. Meanwell, A. Nutton, K. Isobe, A. Vazquez de Miguel, D.W. Bruce, S. Okeya, D.G. Andrews, P.R. Ashton, I.R. Johnstone and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1986) 1565; see also A. Nutton, A. Vazquez de Miguel, K. Isobe and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1983) 166.
16 A. Nutton and P.M. Maitlis, J. Organomet. Chem., 166 (1979) C21.