In memory of T. A. Stephenson

Reactivity of a Cluster-co-ordinated Acyl. Reduction of a μ-Acetyl Ligand to Acetaldehyde *

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The action of HI on the pentanuclear carbido-cluster $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (**1**) affords $Au(PPh_3)I$ and $[Ru_5C(CO)_{14}H(\mu\text{-}MeCO)]$ (**2**). Both (**1**) and (**2**) undergo H^- addition at low temperatures to form unstable formyl compounds which, on raising the temperature, undergo H-shift reactions to generate the hydrido-clusters $[Ru_5C(CO)_{14}H\{Au(PPh_3)\}(\mu\text{-}MeCO)]^-$ and $[Ru_5C(CO)_{14}H_2(\mu\text{-}MeCO)]^-$ respectively. These compounds exist in at least two isomeric forms and on heating decompose to liberate MeCHO.

Much of the interest in the formation of metal acyl species has arisen out of the discussion of their possible role as intermediates in Fischer–Tropsch synthesis.[1–3] The ability of carbonyl clusters to stabilise such ligands as μ-acyls has further prompted their study.[4–7] Cluster-co-ordinated acyls have been synthesised by a variety of methods: (*i*) attack of the appropriate nucleophile R^- on a co-ordinated carbonyl group,[4] (*ii*) coupling of C_2H_4, CO, and a metal hydride,[6] (*iii*) oxidative-addition of RCHO to a suitable precursor material,[7] and (*iv*) by the insertion of ketenes[7] or metal carbynes[8] into a metal–hydrogen bond. We recently described the synthesis of the stable cluster acyl compound $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (**1**)[9] and now wish to report briefly on its reactions with several nucleophilic reagents.

Results and Discussion

Reactions with CO, H_2, *or* I^-.—Potential two-electron donor molecules such as H_2 or CO produce no effect on (**1**) at room temperature; at higher temperatures and pressures (150 °C, 80 atm) although no direct combination is observed, small amounts (~30% Ru conversion) of $[Ru_5C(CO)_{14}\{Au(PPh_3)\}_2]$[9] and $[Ru_6C(CO)_{16}\{Au(PPh_3)\}_2]$[10] (identified on the basis of i.r. and t.l.c.) are produced. In contrast, iodide ions readily react to remove the $\mu\text{-}Au(PPh_3)$ ligand as $Au(PPh_3)I$ and to form the anion $[Ru_5C(CO)_{14}(\mu\text{-}MeCO)]^-$, equation (1).

$$[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)] + I^- \longrightarrow Au(PPh_3)I + [Ru_5C(CO)_{14}(\mu\text{-}MeCO)]^- \quad (1)$$

Subsequent reaction of this anion with a protonic acid affords $[Ru_5C(CO)_{15}]$[11] as the major product together with trace amounts of the hydrido complex $[Ru_5C(CO)_{14}H(\mu\text{-}MeCO)]$ (**2**) in which H^+ addition has occurred directly onto the Ru_5C cage. We find that enhanced yields of (**2**) may be obtained if both steps (nucleophilic addition and protonation) are brought about simultaneously, *e.g.* by passing a stream of HI(g) (I^- + H^+) through a solution of (**1**). On reaction with a non-co-ordinating acid (*e.g.* H_2SO_4) complex (**1**) undergoes protonation without the apparent removal of the $\mu\text{-}Au(PPh_3)$ ligand, the reaction being reversed by the addition of NEt_3. Treatment of a solution of (**1**) with 1,8-diazabicyclo[5.4.0]undec-7-ene affords an uncharacterised anionic species, the reaction being reversed by addition of HBF_4.

	$\delta(^1H)$/p.p.m.	T/°C		$\delta(^1H)$/p.p.m.
(**1**)	7.49 (15 H, m) 2.16 (3 H, s)	−80	(**2**)	2.07 (3 H, s) −20.90 (1 H, s)
	↓ $[BH_4]^-$			↓ $[BH_4]^-$
(**1a**)	14.10 (1 H, s) 7.48 (15 H, m) 2.19 (3 H, s)	−80	(**2a**)	14.11 (1 H, s) 2.08 (3 H, s) −22.00 (1 H, s)
	↓			↓
(**1b**)	7.48 (15 H, m) 2.53 (3 H, s) −19.24 (1 H, s)	−30	(**2b**)	1.94 (3 H, s) −5.27 (1 H, s) —21.79 (1 H, s)
	↓			
(**1c**)	7.49 (15 H, m) 1.32 (3 H, s) −22.16 (1 H, s)	−10		
	↓			↓
(**1d**)	7.50 (15 H, m) 9.75 (1 H, q) 2.16 (3 H, d)	+25		9.74 (1 H, q) 2.16 (3 H, d) + Mixture of hydrido clusters '(**2c**)'

Scheme.

Reactions of (**1**) *and* (**2**) *with* $[BH_4]^-$.—Addition of one equivalent of $[N(PPh_3)_2][BH_4]$ or an excess of $[NEt_4][BH_4]$ to a solution of (**1**) or (**2**) respectively in tetrahydrofuran at room temperature produces the anionic cluster complexes, (**1d**) or '(**2c**)' respectively, together with acetaldehyde (which was identified by ^1H n.m.r.). Complex (**1d**) was identified on the basis of its i.r. spectrum and t.l.c. as $[Ru_5C(CO)_{14}\{Au(PPh_3)\}]^-$ {which may be synthesised directly from $[Ru_5C(CO)_{14}]^{2-}$ and $Au(PPh_3)Cl$} but '(**2c**)' is present (on the basis of ^1H n.m.r.) as a mixture of several metal hydride containing species. In a separate experiment these reactions were monitored by variable-temperature n.m.r. (Scheme, Figure 1); evidence shows the reaction was not simple.

It would appear that the site of the initial attack by the 'H^-'

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* *Non-S.I. unit employed:* atm = 101 325 N m^{-2}.

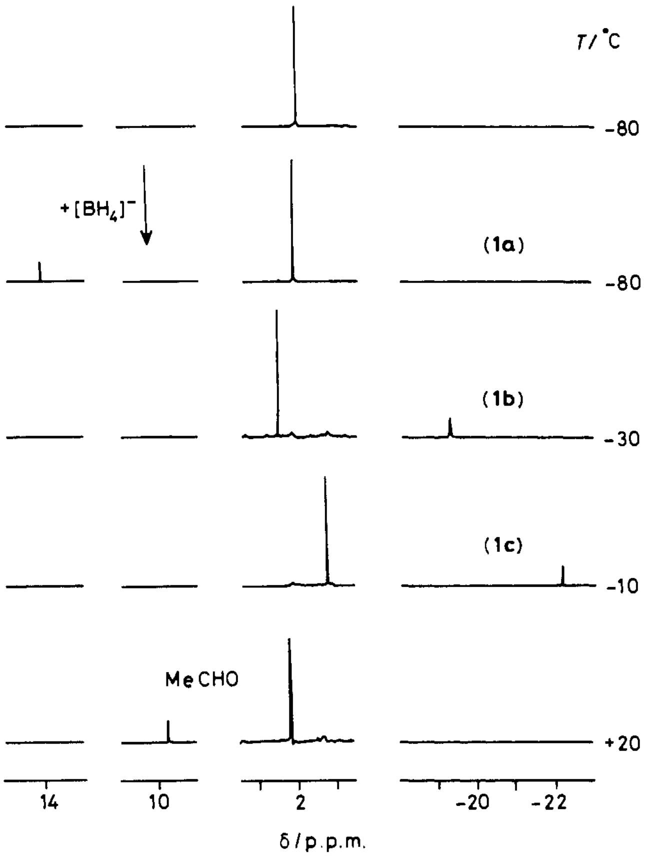

Figure 1. ^{1}H N.m.r. spectra for the reaction of (**1**) with $[BH_4]^-$

nucleophile is at a co-ordinated CO group and that subsequent migration of the hydrido ligand to the metal cage occurs (Scheme).

Addition of $[BH_4]^-$ at −80 °C to a solution of (**1**) in CD_2Cl_2 produces the formyl complex $[Ru_5C(CO)_{13}(CHO)\{Au(PPh_3)\}(\mu\text{-}MeCO)]^-$ (**1a**), which was identified by a typical low-field -C*H*O resonance at δ 14.10 in the ^{1}H n.m.r. spectrum.[12] On warming to −30 °C a rearrangement occurs; the H ligand migrates from the carbonyl group to the central cluster unit, generating the new metal hydride complex $[Ru_5C(CO)_{14}H\{Au(PPh_3)\}(\mu\text{-}MeCO)]^-$ (**1b**) which displays a ^{1}H n.m.r. signal characteristic of a bridging metal hydride. The instability of (**1a**) towards such a rearrangement is typical[12] of many transition metal and cluster based formyls although some are reported[13] to be relatively stable even at elevated temperatures. At −10 °C a second isomer, (**1c**), which on the basis of its ^{1}H n.m.r. also contains a bridging hydride, is observed.

Finally, as the temperature is raised further (> −10 °C) acetaldehyde is liberated. Similar conversions have been reported for a mononuclear molybdenum complex[14] and certain triosmium clusters[4] although in the latter case production of aldehydes is by oxidative addition of a C–H bond rather than by metal hydride attack.

The location of the hydride in (**1b**) and (**1c**) cannot be established by spectroscopic data alone. However, the absence of phosphorus–hydrogen coupling in (**1b**) and (**1c**) suggests that the hydride bridges either Ru(3)–Ru(5) or Ru(4)–Ru(5) [a phosphorus–carbon coupling to the unique carbonyl bonded to Ru(2) was observed in the ^{13}C-{^{1}H} n.m.r. spectrum]. The chemical shift of the methyl resonance in (**1c**) is more in keeping with that of a CH_3 group bonded to an sp^3 carbon, in contrast to the typical acyls (**1**), (**1a**), and (**1b**). This change in chemical shift from (**1b**) to (**1c**) may therefore be due to a change in co-ordination from μ-MeCO to μ_3-MeCO (Figure 2). Attempts to follow the process by ^{13}C n.m.r. were hampered by the low solubility of the complexes together with apparent fluxional behaviour of (**1b**), (**1c**), and (**1d**). Thus, only (**1**) and (**1a**) were characterised by this method.

Complex (**2**) also yielded a formyl derivative, $[Ru_5C(CO)_{13}H(CHO)(\mu\text{-}MeCO)]^-$ (**2a**), on treatment with $[BH_4]^-$; this also undergoes rearrangement to the hydrido species $[Ru_5C(CO)_{14}H_2(\mu\text{-}MeCO)]^-$ (**2b**) at temperatures above −30 °C. However, complex (**2b**) exhibits a metal–hydride signal at an unusually low field (−5.27 p.p.m.) for a high-nuclearity carbonyl cluster, lying within the range usually found for terminally bound metal hydrides. The isomer (**2b**) is stable up to room temperature when acetaldehyde is liberated. No hydrogen–hydrogen coupling is observed for (**2b**), indicating that the low-field hydride is not associated with Ru(1) or Ru(2).

It would appear that whereas the site of 'H^-' attack in both (**1**) and (**2**) is initially at a carbonyl ligand, the subsequent behaviour of the H ligand has been altered considerably by substitution of a μ-Au(PPh$_3$) by a μ-H moiety.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer and mass spectra on a A.E.I. MS12 spectrometer. N.m.r. spectra were recorded on either a Bruker WH-400, WM-250, or WP-80 instrument using a deuterium lock.

Reactions were performed using freshly distilled solvents and under an atmosphere of nitrogen using standard Schlenk techniques. Thin-layer chromatography was performed using precoated silica gel 60 F-254 plates supplied by Merck.

I.r. data refer to ν(CO)/cm^{-1}. N.m.r. data are reported using the chemical shift (δ) scale in units of p.p.m. relative to $SiMe_4$.

Preparation of $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (**1**) *and* $[Ru_5C(CO)_{14}H(\mu\text{-}MeCO)]$ (**2**).—(*a*) $[Ru_5C(CO)_{15}]$ + LiMe + Au(PPh$_3$)Cl. A solution of $[Ru_5C(CO)_{15}]$ (100 mg) in Et_2O (20 cm^3) was cooled to −78 °C. A solution of LiMe in Et_2O (*ca.* 0.1 mol dm^{-3}) was added dropwise until no starting material could be detected by i.r. spectroscopy. The solution was slowly warmed to room temperature and filtered {to remove small amounts of $Li_2[Ru_5C(CO)_{14}]$}; i.r. (Et_2O): 2 070m, 2 043s, 2 029s, 2 007s, and 1 984w br cm^{-1}.

One equivalent of Au(PPh$_3$)Cl was added to the solution at room temperature and after stirring for 1 h the reaction mixture was purified by t.l.c. [acetone–hexane (25:75)] yielding two products: R_f = 0.80, $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (**1**) (5%); R_f = 0.42, $[Ru_5C(CO)_{14}\{Au(PPh_3)\}_2]$ (30%).

(*b*) $[Ru_5C(CO)_{15}]$ + Au(PPh$_3$)Me. To a stirred solution of $[Ru_5C(CO)_{15}]$ (20 mg) in Et_2O (30 cm^3) one equivalent of Au(PPh$_3$)Me was added. After 2 h the solvent was removed under vacuum and the residue purified by t.l.c. [dichloromethane–hexane (50:50)] yielding $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (**1**) (80%); i.r. (CH_2Cl_2): 2 095m, 2 055m, 2 050s, 2 034s, 2 018m, 2 000m, and 1 988m cm^{-1}; n.m.r. (CD_2Cl_2), ^{1}H: δ 7.49 (15 H, m) and 2.16 (3 H, s); ^{13}C-{^{1}H}: δ 460.7 (1 C, s), 308.1 (1 C, s), 205.3 (2 C, s), 200.0 (2 C, s), 197.8 (2 C, s), 194.0 (2 C, s), 193.0 (1 C, s), 191.8 (2 C, s), 190.6 (2 C, s), and 188.9 (1 C, d, $^3J_{P-C}$ 34 Hz) (Found: C, 29.65; H, 1.25. Calc. for $C_{35}H_{18}AuO_{15}PRu_5$: C, 29.75; H, 1.5%).

(*c*) $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (**1**) + HI. A slow stream of HI(g) was bubbled through a solution of $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (100 mg) in CH_2Cl_2 (30 cm^3). After *ca.* 1 min the colour of the solution changed from orange to yellow and the addition of HI was stopped. The solvent was removed under vacuum and the residue extracted with hexane to give a solution of $[Ru_5C(CO)_{14}H(\mu\text{-}MeCO)]$ (80%). This

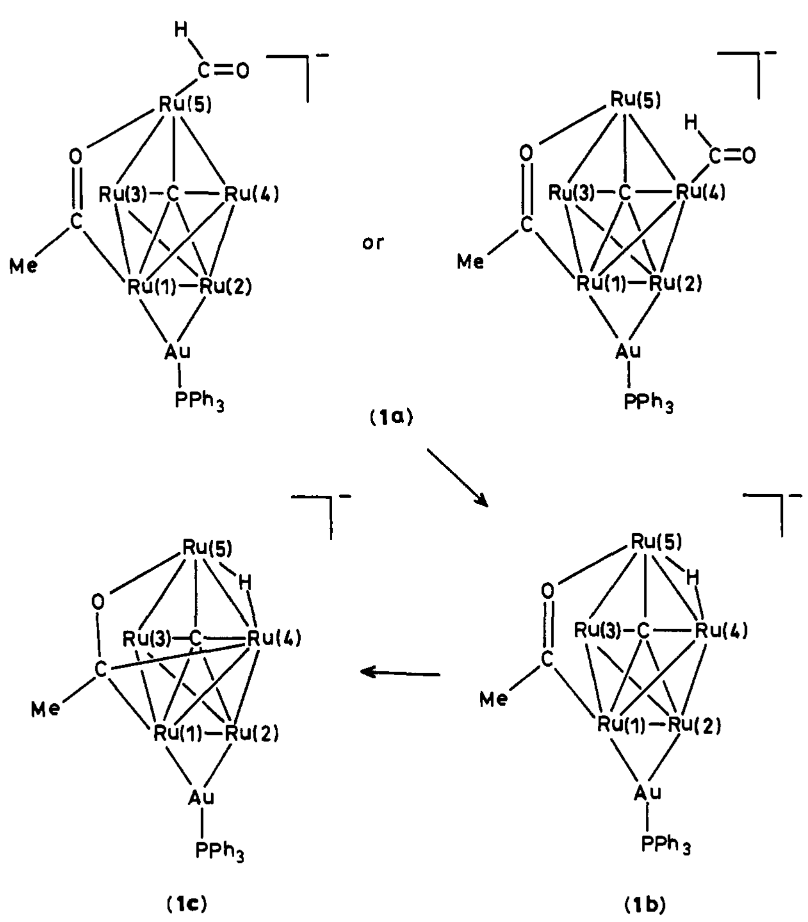

Figure 2. Possible structures of (1a), (1b), and (1c)

solution was further purified by t.l.c. [dichloromethane–hexane (20:80)] to yield a yellow powder: R_f = 0.40, [$Ru_5C(CO)_{14}H(\mu\text{-}MeCO)$] (2); i.r. (hexane): 2 106w, 2 079m, 2 060s, 2 054m, 2 035m, 2 018m, 2 013m, 2 003w, 1 994w, and 1 974w cm^{-1}; n.m.r. (CD_2Cl_2), ^1H: δ 2.07 (3 H, s) and −20.90 (1 H, s); ^{13}C: δ 453.4 (1 C, s), 304.3 (1 C, s), 201.8 (2 C, s), 196.5 (2 C, s), 196.4 (2 C, d, $^2J_{H-C}$ 5 Hz), 193.7 (2 C, s), 193.2 (1 C, s), 191.7 (2 C, s), 190.4 (2 C, s), and 188.3 (1 C, d, $^2J_{H-C}$ 25 Hz) (Found: C, 21.55; H, 0.70. Calc. for $C_{17}H_4O_{15}Ru_5$: C, 21.40; H, 0.40%). Highest mass multiplet *m/z* 953 (^{101}Ru).

(*d*) [$Ru_5C(CO)_{15}$] + LiMe + H^+. As for (*a*) except HBF_4 (3 drops) was added instead of Au(PPh_3)Cl. The i.r. spectrum of the resulting solution showed mainly [$Ru_5C(CO)_{15}$]. The solvent was removed under vacuum and the residue extracted with hexane to give a solution of [$Ru_5C(CO)_{15}$] (confirmed by i.r., spot t.l.c., and mass spectra).

Pyrolysis of [$Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)$] (1).—(*a*) *Under* N_2. A solution of [$Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)$] (30 mg) in toluene (30 cm^3) was heated to 120 °C for 6 h under N_2 (1 atm). The solvent was removed under vacuum and the residue purified by t.l.c. [dichloromethane–hexane (20:80)] yielding two main products: R_f = 0.23, [$Ru_6C(CO)_{16}\{Au(PPh_3)\}_2$] (30%); R_f = 0.16, [$Ru_5C(CO)_{14}\{Au(PPh_3)\}_2$] (25%).

(*b*) *Under* C_2H_4. As for (*a*) except T = 150 °C, P = 30 atm H_2. T.l.c. afforded only [$Ru_6C(CO)_{16}\{Au(PPh_3)\}_2$].

(*c*) *Under* H_2. As for (*a*) except T = 80 °C, P = 30 atm H_2. T.l.c. afforded only [$Ru_5C(CO)_{14}\{Au(PPh_3)\}_2$].

(*d*) *Under* CO. As for (*a*) except T = 100 °C, P = 50 atm CO. No change in the i.r. spectrum was observed.

Reaction with 1,8-*Diazabicyclo*[5.4.0]*undec*-7-*ene*.—[$Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)$] (1) (20 mg) in tetrahydrofuran (thf) (10 cm^3) was treated with one drop of 1,8-diazabicyclo-[5.4.0]undec-7-ene; i.r. (thf): 2 065w, 2 034s, 2 015s, and 1 989m cm^{-1}. To this solution one drop of HBF_4 was added and the reaction mixture stirred for 30 min. Purification by t.l.c. [dichloromethane–hexane (50:50)] afforded two complexes: R_f = 0.75, [$Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)$] (20%); R_f = 0.40, [$Ru_5C(CO)_{14}\{Au(PPh_3)\}_2$] (32%).

Reaction with H^+.—To a stirred solution of [$Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)$] (1) (10 mg) in CH_2Cl_2 (5 cm^3) 10 drops of concentrated H_2SO_4 were added. A slow reaction took place which was complete after 24 h. Distilled water (2 × 3 cm^3) was added, to remove excess H_2SO_4, and the dark red CH_2Cl_2 layer was separated and dried over $MgSO_4$ (yield 20%); i.r. (CH_2Cl_2): 2 108w, 2 082m, 2 063s, and 2 057s cm^{-1}. To this solution one drop of NEt_3 was added and the mixture stirred for 1 h. The i.r. spectrum exhibited only peaks for the starting material (1), and purification by t.l.c. [dichloromethane–hexane (50:50)] yielded one complex: R_f = 0.70, (1) (70%).

Reactions with [BH_4]$^-$.—(*a*) [$Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)$] (1) + [$N(PPh_3)_2$][$BH_4$]. To a stirred solution of [$Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)$] (20 mg) in thf (10 cm^3) one equivalent of [$N(PPh_3)_2$][BH_4] was added. The colour of the solution changed immediately from orange to red, the i.r. spectrum and spot t.l.c. indicating formation of $[Ru_5C(CO)_{14}\{Au(PPh_3)\}]^-$ (**1d**).

(*b*) $[Ru_5C(CO)_{14}H(\mu\text{-}MeCO)]$ (**2**) + $[NEt_4][BH_4]$. To a stirred solution of $[Ru_5C(CO)_{14}H(\mu\text{-}MeCO)]$ (5 mg) in thf (10 cm^3) an excess of $[NEt_4][BH_4]$ was added. After 10 min the reaction was complete; i.r. (thf): 2 070w, 2 027s, 2 008s, 1 993w, and 1 972m cm^{-1}. The reaction mixture was filtered to remove excess $[NEt_4][BH_4]$, the solvent removed under vacuum, and CH_2Cl_2 added. The i.r. spectrum was unchanged but the reaction mixture decomposed under N_2 over a period of *ca.* 1 h. Removal of the solvent under vacuum produced a red powder, '**2c**'. The air-sensitive nature of this solid prevented reliable analysis being obtained.

(*c*) $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (**1**) + $[BH_4]^-$ *at* −78 °C. A solution of $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ (10 mg) in CD_2Cl_2 (1 cm^3) was cooled to −80 °C in the n.m.r. probe. The sample was removed from the probe, placed in an acetone–CO_2(s) bath (−78 °C), and one equivalent of $[N(PPh_3)_2][BH_4]$(s) added under an atmosphere of N_2. The sample was returned to the pre-cooled probe and ^1H n.m.r. spectra recorded as the sample was allowed to warm to room temperature over a period of 7 h.

For the ^{13}C n.m.r. experiment the same procedure was followed except that 100 mg of $[Ru_5C(CO)_{14}\{Au(PPh_3)\}(\mu\text{-}MeCO)]$ was used.

The product formed was $[Ru_5C(CO)_{13}(CHO)\{Au(PPh_3)\}(\mu\text{-}MeCO)]^-$ (**1a**); n.m.r. (CD_2Cl_2), ^1H: δ 14.10 (1 H, s), 7.48 (15 H, m), and 2.19 (3 H, s); $^{13}C\text{-}\{^1H\}$ (carbonyl): δ 302.8 (1 C, s), 250.1 (1 C, s), 209.7 (1 C, s), 209.1 (1 C, s), 204.0 (1 C, s), 203.8 (1 C, s), 202.4 (1 C, s), 201.8 (1 C, s), 201.2 (1 C, s), 199.0 (1 C, s), 198.7 (1 C, s), 197.4 (1 C, s), 197.0 (1 C, s), 194.5 (1 C, s), and 191.6 (1 C, d, $^3J_{P-C}$ 24 Hz).

Acknowledgements

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