Formation of acylruthenium promoted by coordination of AlMe₃ to $(\eta^4$ -cyclopentadienone)Ru(CO)₃†

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The reaction of AlMe₃ with (η^4 -tetraphenylcyclopentadienone)Ru(CO)₃ leads to rapid and quantitative formation of an adduct arising from coordination of the enone oxygen to aluminium, which undergoes alkylation at the Ru(CO)₃ moiety to give (η^5 -C₄Ph₄C(OAlMe₂))Ru(CO)₂(COMe) concomitant with a change of hapticity of the dienone ligand.

Although reaction of transition metal carbonyl complexes with alkyllithium or alkylmagnesium gives acylate complexes by alkylation of carbon monoxide on the transition metal,¹ less nucleophilic alkylmetal reagents do not react with transition metal carbonyl complexes under similar reaction conditions. Thus, a new method for enhanced reactivity between transition metal carbonyl complexes and less nucleophilic alkylmetal reagents is required. One solution to this issue is suggested by the observation that a trialkylaluminium can undergo alkylation of the enone to give a conjugate addition product in the presence of a transition metal catalyst. As one possible reaction mechanism, we proposed that the coordination of alkyl metals to the carbonyl group in the enone triggered oxidative bond formation between the transition metal center and the terminal carbon of α , β -unsaturated carbonyl compounds, facilitating alkyl group transfer.² From this point of view, we assumed that an η^4 -cyclopentadienone ruthenium carbonyl complex would confirm if alkylation of a carbonyl ligand with alkylaluminium is possible. In fact, it has been proposed that inter-exchange of hapticity between η^4 and η^5 by coordination of a Brønsted acid to oxygen plays an important role in catalytic hydrogenation of unsaturated compounds.3 Therefore, formation of a Lewis acid-cyclopentadienone complex would generate an n⁵cyclopentadienyl group accompanied by enhanced electrophilicity of the M-CO moiety. Here, we wish to report the reaction of (n⁴-tetraphenylcyclopentadienone)Ru(CO)₃ with alkylaluminium compounds, leading to the formation of acylruthenium complexes triggered by the coordination of alkylmetal compounds to the carbonyl oxygen of cyclopentadienone.

The reaction of $(\eta^4$ -TPCPD)Ru(CO)₃ (1) (TPCPD = tetraphenylcyclopentadienone) with aluminium compounds quantitatively gave the corresponding coordination products (Scheme 1, **2a**: AlMe₂Cl, **2b**: AlMeCl₂, **2c**: AlCl₃). The extent to which the zwitterionic η^5 -structure (Fig. 1) contributes to complexes **2a**, **2b** and **2c** could be estimated from the



Fig. 1 Zwitterionic η^5 -structure.

comparison of ¹³C NMR and IR spectra with those of $[(\eta^5$ hydroxytetraphenylcyclopentadienyl)Ru(CO)₃[[OTf] (3) (Fig. 2), which was prepared by the reaction of 1 with CF₃SO₃H and identified as having the n⁵-structure by X-ray crystallography. As a result of coordination of the carbonyl oxygen of 1 to aluminium compounds, the CO stretching absorption of the coordinated carbon monoxide in the infrared spectrum moved to a higher wavenumber, and the resonance of the carbonyl carbon in the TPCPD group moved to higher magnetic field in the ¹³C NMR spectrum (Table 1). Moreover, these parameters progressively approached those of 3 with increasing acidity of the aluminium compounds. The above observation indicates that coordination of the aluminium compounds increases electron donation from ruthenium to TPCPD ligands. The positive charge on ruthenium inhibits back donation to carbon monoxide. A similar influence on a palladium-bound enone ligand by coordination of a Lewis acid to enone oxygen was rationalized based on the MO calculation.²



The reaction of $(\eta^4$ -TPCPD)Ru(CO)₃ **1** with 1 equiv of AlMe₃ was also carried out. In the early stage of the reaction, quantitative formation of the intermediate complex (**2d**) (Scheme 2) could be deduced by observation of a doublet peak at δ 7.50 in C₆D₆ in ¹H NMR. This doublet corresponds to the *ortho* protons of 2- and 5- phenyl groups of the TPCPD ligand. The appearance of the peak in this region seems to be indicative of coordination of AlX₃ to the carbonyl group in TPCPD; the *ortho* proton was observed at

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Complex	Additive	$\delta_{\rm C=O}~({\rm ppm})^a$	$v_{\rm C=O}/{\rm cm}^{-1b}$
1	none	173.0	2080, 2029, 2004
2a	AlMe ₂ Cl	158.1	2104, 2056, 2035
2b	AlMeCl ₂	155.1	2109, 2059, 2041
2c	AlCl ₃	150.8	2111, 2061, 2042
3	TfOH	148.6	2120, 2070,
			2050 ^c

^a CDCl₃. ^b C₆H₆. ^c KBr.



Scheme 2 Formation of acylruthenium complex.

 δ 7.48 in 1, δ 7.56 in 2a, δ 7.55 in 2b and δ 7.50 in 2c. Complex 2d easily underwent alkylation of carbon monoxide to quantitatively give the expected acylruthenium complex (4). The spectrum of 4 in C₆D₆ showed the following characteristic signals: resonance at 289.8 ppm for acyl carbon in ¹³C NMR; the singlet at 2.36 ppm corresponds to CH₃ in acyl groups in ¹H NMR; and the signal at -0.55 ppm was assigned to OAlMe₂ in ¹H NMR.

Protonolysis of 4 gave the corresponding acylruthenium complex (5),[‡] the structure of which was determined by X-ray crystallography (Scheme 3, Fig. 3). The short distance between two oxygen atoms (2.54 Å) indicates the presence of hydrogen bonds.⁴ The reaction of 5 with AlMe₃ regenerated 4 quantitatively, which is also consistent with the structure of 4. The resonances of carbonyl carbon in the acyl group (δ 289.8) and alumoxy-substituted carbon in the cyclopentadienyl ring (δ 141.3) in 4 appear at lower magnetic fields than those (δ 252.1, 130.5) in 5. This observation can be



Scheme 3 Hydrolysis of 4.



Fig. 3 Molecular structure of 5 with thermal ellipsoids at the 30% probability level. Phenyl groups and hydrogen atoms except for H1 are omitted for clarity. The location of the H1 hydrogen at O1 unequivocally established the existence of an intramolecular O1–H1 \cdots O2 hydrogen bond.

explained by the contribution of alumoxy-substituted carbene structure 4' to 4. The range of chemical shifts of usual carbene carbons in transition metal carbene complexes occurs at a lower magnetic field than that of acyl carbons in acyl complexes.⁵

As mentioned above, the coordination complex **2d** is generated quantitatively during the early stage of the reaction shown in Scheme 2. Thus, the decrease in the coordination complex **2d** was followed using ¹H NMR. The plot of $-\ln([2d]/[2d_0])$ vs. time gave a straight line over four half-lives. Almost identical k_{obs} were obtained for three different concentrations of **1** in the presence of 1 equiv of AlMe₃ (= **2d**) ([**2d**₀] = 1.46 × 10⁻² M, $k_{obs} = 2.2 × 10^{-3} \text{ s}^{-1}$; [**2d**₀] = 2.93 × 10⁻² M, $k_{obs} = 2.3 × 10^{-3} \text{ s}^{-1}$; [**2d**₀] = 5.85 × 10⁻² M, $k_{obs} = 2.4 × 10^{-3} \text{ s}^{-1}$). These observations indicate that the reaction proceeds in an intramolecular manner. For comparison, the reaction of (η⁴-cyclohexadiene)Ru(CO)₃⁶ with AlMe₃ did not proceed at all, while AlMe₃ reacted with [CpRu(CO)₃][OTf]⁷ very slowly to give the corresponding acylruthenium complex, as well as a small amount of methylruthenium complex⁸ (Scheme 4).



Scheme 4 Control experiment.

The alkylation reaction might proceed as follows (Scheme 5). The coordination of AlMe₃ to carbonyl oxygen occurs very rapidly to generate coordination complex 2d. Then, the electron density on the ruthenium center is reduced by AlMe₃ coordination to TPCPD, resulting in the formation of zwitterionic intermediate A. Then, direct nucleophilic attack of the carbon monoxide might occur, since the nucleophilicity of the methyl group on aluminium and the electrophilicity of the Ru-CO ligand are enhanced due to the zwitterionic form. Alternatively, transmetallation might proceed more readily, concomitant with slippage of the cyclopentadienyl ring. Then, insertion of carbon monoxide would generate a 16-electron acyl complex followed by ring slippage to give the acyl complex 4. In general, alkyllithium and Grignard reagents have been used for nucleophilic alkylation of metal carbonyls.⁸ Therefore, the types of functional group that can co-exist in nucleophilic alkylation of metal carbonyl are limited. In contrast, AlMe₃ is more tolerant of a wide variety of functional groups. Thus, the development of this reaction system into a general



Scheme 5 Plausible mechanism.

method that is applicable to other alkylmetals would expand the utility of the carbonylation reaction in organic synthesis.

In conclusion, we demonstrated the formation of an acyl complex by the reaction of $(\eta^4$ -TPCPD)Ru(CO)₃ with AlMe₃. In this reaction, the most important step appears to be the coordination of alkylmetal compounds to the carbonyl oxygen of the TPCPD ligand. The Lewis acidity of alkylaluminium compounds induces a positive charge on the ruthenium center, which generates the zwitterionic intermediate. As a result, the carbonylation reaction proceeds smoothly.

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Notes and references

[‡] To a solution of (n⁴-C₄Ph₄C=O)Ru(CO)₃ (200 mg, 0.351 mmol) in 10 mL of toluene was added 370 µL (1.0 M) of a solution of AlMe₃ (0.370 mmol) in n-hexane at room temperature. After 1 h, aqueous HCl (5 mL, 1.0 N) was added to the solution and the mixture was stirred for 30 min at room temperature. The solution was dried (MgSO₄), filtered, and concentrated in vacuo to give a yellow solid quantitatively. The solid was washed with n-hexane and dried in vacuo to give a yellow solid 5 (194 mg, 94%). An analytical sample was prepared by recrystallization from C₆H₆-n-hexane solution. ¹H NMR (C₆D₆, 400 MHz): δ 2.45 (s, 3H) 6.80–6.81 (m, 6H), 6.88-6.95 (m, 6H), 7.11 (dd, J = 7.6, 8.0 Hz, 4H), 7.45 (d, J = 6.4 Hz, 4H), 10.5 (s, 1H). ¹³C NMR (C₆D₆, 100 MHz): δ 50.8 (COCH₃), 96.8 (C 3,4 of Cp), 107.0 (C 2,5 of Cp), 130.2–133.8 (aromatic), 202.2 (CO), 250.4 (COCH₃). ¹H NMR (CDCl₃, 400 MHz): δ 2.76 (s, 3H), 7.00–7.02 (m, 4H), 7.09 (t, J = 7.6 Hz, 4H), 7.15 (d, J = 7.6 Hz, 2H), 7.18–7.21 (m, 10H), 9.72 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 51.1 (COCH₃), 96.5 (C 3,4 of Cp), 106.4 (C 2,5 of Cp), 127.7–132.2 (aromatic), 130.5 (C1 of Cp), 201.3 (CO), 252.1 (COCH₃). Anal. calcd for C₃₃H₂₄O₄Ru: C, 67.68; H, 4.13. Found: C, 67.41; H, 4.23%.

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