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ADAMANTYLCYCLOPENTADIENYLDICARBONYLIRON(II) COMPOUNDS

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Summary

Synthesis of 1- and 2-adamantyl derivatives of η^5-cyclopentadienyldicarbonyliron is reported. The 2-adamantyl is prepared from the metal carbonyl anion but the 1-adamantyl derivative is prepared by decarbonylation of the acyl derivative. 1-AdCOFe$(CO)_2(\eta^5$-$C_5H_5)$ is in turn prepared from 1-AdCOCl and NaFe$(CO)_2(\eta^5$-$C_5H_5)$. Phosphine-substituted acyl derivatives AdCOFe(CO)(PR_3)-$(\eta^5$-$C_5H_5)$ are also reported.

Introduction

In the thermally stable 1-norbornyl compounds [1] nor $_3$M or nor $_4$M the transition metal is bound to a bridgehead carbon and consequently decomposition by way of β-hydrogen transfer to metal is unfavourable. Adamantyl compounds should be equally stable but so far only tetra(1-adamantyl)titanium [2], obtained by interaction of $TiCl_4$ and adamantyl chloride with sodium, in cyclohexane and the 1-adamantylpentacyanocobaltate ion [3] are known. Attempts to synthesize adamantyls by interaction of adamantyllithium and adamantylmagnesium bromide with transition metal halides have failed [4].

Results and discussion

While the classical method [5] of synthesis of metal cyclopentadienyl carbonyl alkyls involves nucleophilic displacement of halogen from an alkyl halide by a carbonylate anion, bridgehead halides such as 1-adamantyl halides are inert to substitution [6] and indeed do not react with $[\eta^5$-$C_5H_5Fe(CO)_2]^-$. The 2-adamantyl halides do so under the usual conditions [6]. The chlorine atom of 1-adamantylcarboxylic acid chloride is not inert to nucleophilic substitution, and hence the adamantyl acyl can be obtained by the reaction [Ad = adamantyl]:

$$\text{1-AdCOCl} + \text{NaFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) \rightarrow \text{1-AdCOFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) + \text{NaCl}$$

The acyl compound crystallises as yellow needles, stable in air for at least three years, sublimable in vacuo [80°C/10^{-3} mmHg] without decomposition, although at slightly higher temperatures minor decarbonylation does occur to afford 1-adamantylcyclopentadienyldicarbonyliron(II):

$$\text{1-AdCOFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) \xrightarrow{\Delta \text{ or } h\nu} \text{1-AdFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) + \text{CO}$$

Although this decarbonylation reaction proceeds slowly, with a low yield on prolonged refluxing of the acyl in heptane, ultra violet irradiation at room temperature in saturated hydrocarbon solvents affords moderate yields of the alkyl together with substantial amounts of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$, probably formed by further photolytic decomposition of the former. The iron dimer, however, may be readily separated from the desired product by its reduced solubility in saturated hydrocarbons, or by column chromatography. The 1-adamantyl crystallises as yellow needles, is stable to sublimation at 80°C/10^{-3} mmHg, and undergoes only superficial oxidation in air over a period of two years, ferrocene being a product of this decomposition.

A decarbonylation reaction of the acyl using $(\text{Ph}_3\text{P})_3\text{RhCl}$ proceeds slowly at room temperature in ether, but moderately rapidly on refluxing in benzene:

$$(\text{Ph}_3\text{P})_3\text{RhCl} + \text{1-AdCOFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) \rightarrow \text{1-AdFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) + \text{Ph}_3\text{P} + (\text{Ph}_3\text{P})_2\text{Rh(CO)Cl}$$

but the triphenylphosphine liberated displaces carbon monoxide from the metal, and yields of $\text{1-AdFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$ were highest after ~1 h, although not all the starting material had been consumed. The main product accordingly was the phosphine-substituted acyl $\text{1-AdCOFe(CO)(Ph}_3\text{P)}(\eta^5\text{-C}_5\text{H}_5)$, which was also prepared independently. It is of interest that $\text{1-AdFe(CO)(PPh}_3)(\eta^5\text{-C}_5\text{H}_5)$ is formed by phosphine substitution of $\text{1-AdFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$ and not by direct substitution of $\text{1-AdCOFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$. Thus the alkyl complex reacts rapidly with triphenylphosphine on warming in benzene solution whereas the acyl complex reacts only very slowly and is incomplete even after refluxing in benzene for 1 week. The difference in rates of CO substitution by PPh_3 of the alkyl and the acyl is evidently caused by alkyl migration of the 1-adamantyl group in the alkyl giving a vacant coordination site for the incoming phosphine. Similarly pivaloylcyclopentadienyldicarbonyliron can be decarbonylated by $\text{RhCl(PPh}_3)_3$ to the t-butyl [7] though in low yield. The phosphine-substituted t-butyl acyl was obtained in good yield by the reaction:

$$\text{t-BuCOFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5) + \text{RhCl(PPh}_3)_3 \rightarrow \text{t-BuCOFe(CO)(PPh}_3)(\eta^5\text{-C}_5\text{H}_5) + \text{RhCl(CO)(PPh}_3)_2$$

2-Bromoadamantane reacts with $\text{NaFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$ to give only low yields of 2-AdFe(CO)$_2$(η^5-C$_5$H$_5$) over two days at room temperature. Like the 1-adamantyl, 2-AdFe(CO)$_2$(η^5-C$_5$H$_5$) is a yellow crystalline, sublimable [80°C/ 10^{-3} mmHg] moderately air-stable compound, that reacts readily with triphenylphosphine to afford the red-orange acyl, 2-AdCOFe(CO)(Ph$_3$P)(η^5-C$_5$H$_5$).

Infrared carbonyl stretching frequencies and analytical data are given in Table 1.

2-AdFe(CO)$_2$(η^5-C$_5$H$_5$) is readily converted to 2-AdCOFe(CO)$_2$(η-C$_5$H$_5$) by heating under reflux in heptane and bubbling carbon monoxide through the solution.

Experimental

Tetrahydrofuran was purified by distillation from sodium diphenylketyl just prior to use. Saturated hydrocarbons and benzene were stored over sodium wire.

Adamantane carboxylic acid chloride was sublimed just prior to usage.

Elemental analyses from the microanalytical laboratories of Imperial College.

1-Adamantylcarbonyl-η^5-cyclopentadienyldicarbonyliron(II)

To a solution of sodium cyclopentadienyldicarbonylferrate (20 mmole) in THF (100 cm^3) was added dropwise with stirring a solution of 1-adamantane carboxylic acid chloride (3.97 g, 20 mmole) dissolved in THF (25 cm^3). A mildly exothermic reaction occurred accompanied by a pronounced lightening in colour of the reaction mixture. After stirring at ambient temperature for 2 h solvent was removed in vacuo, an orange residue remaining. This was digested with several portions of hot pentane until the extracts were no longer coloured. Removal of solvent from these extracts followed by recrystallisation from hexane afforded the product (6.21 g, 91%) as bright yellow needles, m.p. 149.5-150.5°C).

1-Adamantyl-η^5-cyclopentadienyldicarbonyliron(II)

A solution of 1-adamantylcarbonylcyclopentadienyldicarbonyliron(II) (3.40 g, 10 mmole) dissolved in pentane (200 cm^3) was irradiated in a Hanovia 1L photochemical reactor with a medium pressure lamp. After 15 min at ambient temperature the solution had darkened considerably. Monitoring of the reaction mixture by infrared spectroscopy indicated that all the starting material had been destroyed, an approximately 1/1 mixture of the product and bis(cyclopentadienyldicarbonyliron) being present. Further irradiation resulted only in gradual decomposition of the product with consequent formation of more bis(cyclopentadienyldicarbonyliron). Solvent was removed, a purple brown residue remaining. This was digested with pentane/ether (10/1) (10 cm^3), filtered and the filtrate chromatographed on alumina. The yellow band was eluted with pentane/ ether (4/1) and collected under nitrogen. Removal of solvent from this resulted in the deposition of yellow crystals which are sublimed (60°C/10^{-3} mmHg) to afford the yellow, air-stable product (1.22 g, 39%), m.p. 93-94°C.

2-Adamantyl-η^5-cyclopentadienyldicarbonyliron(II)

To a solution of sodium cyclopentadienyldicarbonylferrate (20 mmole)

TABLE 1

PHYSICAL PROPERTIES, ANALYSES AND INFRARED CARBONYL STRETCHES FOR THE COMPOUNDS

Compound	Colour	m.p. (°C)	Analyses found (calcd.) (%)				ν(M—CO) [a] (cm^{-1})	ν(M—CO—R) (cm^{-1})
			C	H	P	Fe		
1-AdFe(CO)$_2$(η^5-C$_5$H$_5$)	Yellow	93-94	65.3 (65.4)	6.5 (6.4)		18.0 (17.9)	1999(8.0), 1945(10)	
1-AdCOFe(CO)$_2$(η^5-C$_5$H$_5$)	Yellow	149.5-150.5	63.4 (63.5)	5.9 (5.9)			2015(7.7), 1954(10)	1652, 1633(sh)
2-AdFe(CO)$_2$(η^5-C$_5$H$_5$)	Yellow	107-108	65.4 (65.4)	6.5 (6.4)		18.1 (17.9)	1998(9.8), 1942(10)	
2-AdCOFe(CO)$_2$(η^5-C$_5$H$_5$)	Yellow	97-99	63.7 (63.5)	5.9 (5.9)			2014(7.7), 1955(10)	1668, 1651(sh)
1-AdCOFe(CO)(Me$_3$P)(η^5-C$_5$H$_5$)	Orange-red	200 (dec.)	61.7 (61.9)	7.3 (7.5)	7.6 (8.0)		1909	1591
1-AdCOFe(CO)(Ph$_3$P)(η-C$_5$H$_5$)	Red	176-177	72.5 (73.2)	6.1 (6.1)	5.9 (5.4)		1915	1598
2-AdCOFe(CO)(Ph$_3$P)(η-C$_5$H$_5$)	Orange-red	176-177	73.0 (73.2)	6.2 (6.1)	5.8 (5.4)		1917	1608

[a] Relative intensities of the carbonyl stretches are given in parentheses.

was added dropwise with stirring a solution of 2-bromoadamantane (4.30 g, 20 mmole) dissolved in THF (25 cm^3). The reaction mixture was stirred at ambient temperature for 2 days. Solvent was removed in vacuo, and the brown residue digested with hot cyclohexane (20 cm^3). Chromatography of the cooled extracts on alumina afforded a yellow band of product when eluted with cyclohexane/benzene (80/20). This was collected, solvent was removed in vacuo, and the residue sublimed to afford the yellow compound (0.67 g, 11%), m.p. 107-108°C.

2-Adamantylcarbonyl-η^5-cyclopentadienyldicarbonyliron(II)

Through a solution of 2-amantylcyclopentadienyldicarbonyliron(II) (0.312 g, 1 mmole) in boiling heptane was bubbled carbon monoxide until infrared monitoring showed the reaction was complete (ca. 2 h). Solvent was removed leaving a yellow solid, which was sublimed at 75°C/10^{-1} mmHg to afford the pale yellow product, m.p. 97-99°C (0.33 g, 97%).

1-Adamantyl-η^5-cyclopentadienyldicarbonyliron(II) from 1-adamantylcarbonyl-η^5-cyclopentadienyldicarbonyliron(II) and tris(triphenylphosphine)chlororhodium(I)

A mixture of 1-adamantylcarbonyl cyclopentadienyldicarbonyliron(II) (0.34 g, 1 mmole) and tris(triphenylphosphine)chlororhodium (1.85 g, 2 mmole) in benzene (15 cm^3) was stirred * at room temperature for 1 h. The mixture was then filtered, solvent removed, and the residue digested in hexane/benzene (60/40) (10 cm^3). Chromatography on alumina using hexane/benzene (3/2) afforded first a yellow band of 1-adamantylcyclopentadienyldicarbonyliron(II), which was collected and purified by removal of solvent followed by sublimation (80°C/10^{-3} mmHg) (0.046 g, 15%), followed by an orange band of 1-adamantylcarbonyltriphenylphosphinecyclopentadienylmonocarbonyliron(II). Removal of solvent from this, followed by recrystallisation from heptane, afforded red crystals of the compound (0.072 g, 13%), m.p. 176-177°C.

1-Adamantylcarbonyl-triphenylphosphine-η^5-cyclopentadienylmonocarbonyliron(II)

A mixture of 1-adamantylcyclopentadienyldicarbonyliron(II) (0.312 g, 1 mmole) and triphenylphosphine (0.262 g, 1 mmole) was heated under reflux in benzene (10 cm^3) for ½ h. Infrared monitoring of the reaction mixture indicated that all starting materials had been consumed. Solvent was removed in vacuo and the red crystalline residue was washed with several 3 cm^3 portions of cold pentane, and air dried. Yield 0.56 g, (98%, m.p. 175-177°C).

1-Adamantylcarbonyl-triphenylphosphine-η^5-cyclopentadienylmonocarbonyliron(II) from 1-adamantylcyclopentadienyldicarbonyliron(II)

A mixture of 1-adamantylcarbonylcyclopentadienyldicarbonyliron(II) (0.34 g, 1 mmole) and triphenylphosphine (0.262 g, 1 mmole) was heated under reflux in benzene (10 cm^3) for 6 days. Even after this period there remained

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* IR monitoring of the reaction mixture showed that the ratio of 1-AdFe$(CO)_2(\eta\text{-}C_2H_5)$ to 1-AdCOFe(CO)$(Ph_3P)(\eta\text{-}C_5H_5)$ was the highest after this time, although some 1-AdCOFe$(CO)_2(\eta\text{-}C_5H_5)$ remained unconsumed.

unconsumed starting material. Chromatography on alumina of the reaction mixture using benzene as eluent afforded a red band of the product, which was collected and isolated by solvent removal followed by pentane washing (10 cm^3) and air-drying (0.38 g, 66%).

1-Adamantylcarbonyl-trimethylphosphine-η^5-cyclopentadienylmonocarbonyliron(II)

A mixture of 1-adamantylcyclopentadienyldicarbonyliron(II) (0.312 g, 1 mmole) and benzene (10 cm^3) cooled to $-196°C$ and evacuated was condensed in trimethylphosphine (0.11 g, 1.49 mmole). The reaction mixture was allowed to attain room temperature and then heated under reflux for 1 h. Solvent was removed in vacuo and the orange-red residue sublimed ($100°C/10^{-2}$ mmHg) onto a water-cooled probe. Yield (0.37 g, 96%).

Decarbonylation of pivaloyl-η^5-cyclopentadienyldicarbonyliron(II) using tris(triphenylphosphine)chlororhodium(I)

A mixture of pivaloylcyclopentadienyldicarbonyliron(II) (0.262 g, 1 mmole) and tris(triphenylphosphine)chlororhodium(I) (1.85 g, 2 mmole) was heated under reflux in benzene (10 cm^3) for ½ h. After this period solvent was removed and the yellow-brown residue digested with hexane (10 cm^3). Chromatography * using hexane/benzene (10/1) as eluent afforded ferrocene (0.018 g, 19%), t-butylcyclopentadienyldicarbonyliron(II) (trace, identified by comparison of its IR spectrum to that of an authentic sample) and pivaloyltriphenylphosphinecyclopentadienylmonocarbonyliron(II) (0.28 g, 56%).

Pivaloylcyclopentadienyldicarbonyliron(II)

To a solution of sodiumcyclopentadienyldicarbonylferrate(0) (40 mmole) in THF (150 cm^3) was added dropwise with stirring freshly distilled pivaloyl chloride (6.5 g, 54 mmole). After stirring at ambient temperature for 2 h, solvent was removed and the yellow-brown residue was digested with warm hexane. Filtration of the extracts followed by solvent removal and recrystallisation from hexane/benzene (10/1) afforded orange-yellow needles of the product, which were obtained by filtration and drying in vacuo (6.37 g, 61%), m.p. 75-76°C.

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References

1 B.K. Bower and H.G. Tennant, J. Amer. Chem. Soc., 94 (1972) 2512.
2 R.M.G. Roberts, J. Organometal. Chem., 63 (1973) 159.
3 S.H. Goh and L.-Y. Goh, J. Organometal. Chem., 43 (1972) 159.
4 E. Sigurdson and G. Wilkinson, unpublished work.
5 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.

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* Alumina 15 cm × 2 cm column.

6 P. Sykes, A. Guidebook to Mechanisms in Organic Chemistry, 2nd. Ed., John Wiley & Sons, 1965, p. 58.
7 W.P. Giering and M. Rosenblum, J. Organometal. Chem., 25 (1970) C71.