

## [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ]<sub>2</sub>; a Versatile Catalyst for Ligand-replacement Reactions on Transition-Metal Complexes

By NEIL J. COVILLE\* and MICHEL O. ALBERS

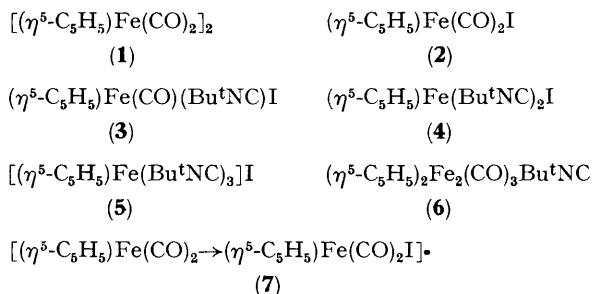
(Department of Chemistry, University of the Witwatersrand, Johannesburg 2001, Republic of South Africa)

and TERENCE V. ASHWORTH and ERIC SINGLETON

(National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001, Republic of South Africa)

**Summary** The compound [ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ ]<sub>2</sub>, in the presence of suitable donor ligands, is found to catalyse the replacement of ligands, such as CO, group 5 donor ligands, and halides, on transition-metal complexes; a non-chain free-radical mechanism for the above reaction is proposed.

RECENT work in our laboratories<sup>1</sup> has suggested that the isonitrile ligand, RNC, may be a useful probe for the investigation of catalytic systems involving free radicals.<sup>2</sup> As an extension of our earlier study we have investigated the use of [ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ ]<sub>2</sub> (**1**) as a catalyst in the substitution of CO, group 5 donor ligands, and halides attached to metal carbonyls or substituted metal carbonyls by RNC. It has been established that the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\cdot$  radical is readily generated from compound (**1**) both thermally<sup>3</sup> and photochemically<sup>4</sup> and the use of (**1**) as a photochemically activated catalyst has been described.<sup>4,5</sup> Further, it was suggested that the substitution reactions catalysed by compound (**1**) proceed *via* a radical-chain mechanism.<sup>4,5</sup>



Reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  (**2**) (1 mmol) and  $\text{Bu}^t\text{NC}$  (1, 2, or 3 mmol) in refluxing benzene, in the presence of compound (**1**) (0.01 mmol) as a catalyst, rapidly gives the new complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{Bu}^t\text{NC})\text{I}$  (**3**) and  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Bu}^t\text{NC})_2\text{I}$  (**4**) and, more slowly, the salt [ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{Bu}^t\text{NC})_3$ ]**I** (**5**) in high yield (60–80%). In the absence of compound (**1**), mixtures of the products (**3**) and (**4**) are obtained in poor yield even after long reaction times. Similar reactions have been carried out with other isonitriles (*e.g.*  $\text{RNC} = 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$ ,  $\text{PhNC}$ ,<sup>6</sup> and  $\text{PhCH}_2\text{-NC}$ ), with group 5 donor ligands [*e.g.*  $\text{PPh}_3$ ,<sup>7</sup>  $\text{P}(\text{OMe})_3$ ,<sup>8</sup> and  $\text{AsMe}_2\text{Ph}$ ], and using  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$  as the substrate.<sup>9</sup> The new products have been completely characterized by *i.r.*, *n.m.r.*, and elemental analysis.

The above reactions were conducted in benzene at a lower temperature (40–45 °C) and gave mechanistic information relating to this catalytic reaction. (i) Reaction of compound (**2**) (0.5 mmol),  $\text{Bu}^t\text{NC}$  (0.5 mmol), and compound (**1**) (0.25 mmol) gave the product (**3**) (>90% yield, 90 min). (ii) The reaction (i) above is inhibited by hydroquinone and galvinoxyl and is strongly dependent on light (irradiation with a 500 W light bulb results in complete reaction in *ca.* 1 min). (iii) The light-induced reaction (500 W light bulb) between compound (**2**) and  $\text{Bu}^t\text{NC}$  gives a slow reaction to produce a mixture of the products (**3**) and (**4**). These results suggest that the catalysed reaction involves free radicals, in keeping with other studies on the use of compound (**1**) as a catalyst.<sup>4,5</sup> This is further suggested by the reaction between [ $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3$ ]<sub>2</sub> and compound (**2**) which yields  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{I}$ ,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{MoFe}(\text{CO})_5$ ,<sup>10</sup> and (**1**).

Further pertinent reactions carried out at 40 °C, however, are not in keeping with the expected radical-chain mechanism.<sup>4,5</sup> Thus, the reaction of compound (**1**) and  $\text{Bu}^t\text{NC}$

(both 0.5 mmol) gives <5% of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{Bu}^t\text{NC}$  (**6**) after 90 min and the reaction of compound (**6**)<sup>11</sup> [a precursor to the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{L}\cdot$  radical<sup>3</sup>] and (**2**) (both 0.5 mmol) also gives <5% of the product (**3**) after 90 min. The catalytic substitution of compound (**2**) by RNC [see (i) above] is thus faster than an indirect radical-chain mechanism involving  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{L}\cdot$ .<sup>4,5</sup> The catalytic synthesis of compound (**5**) from compound (**4**) and the synthesis of compound (**4**) from compounds (**1**), (**3**), and  $\text{Bu}^t\text{NC}$  (equimolar) are also difficult to interpret in terms of a radical-chain mechanism.

We have also observed that the reaction between  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$  and  $\text{Bu}^t\text{NC}$ <sup>6</sup> is catalysed by compound (**1**) to yield the products (**3**), (**4**), and  $\text{PPh}_3$ . Irradiation was found to increase the reaction rate dramatically. Thus, catalytic substitution of ligands other than CO can also be achieved by RNC.

A more plausible explanation is in terms of a non-chain radical mechanism in which  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\cdot$ , generated from the catalyst (**1**), attacks compound (**2**) to give the intermediate (**7**). This intermediate (**7**) is activated

towards ligand dissociation in the presence of suitable donor ligands *via* what is thought to be an associative mechanism (qualitative kinetic data suggest that the reaction is dependent on the nature of the incoming ligand). The exact nature of intermediate (**7**) is unknown, but it must allow for ligand exchange between metal centres under suitable conditions.<sup>4</sup>

The non-chain nature of the radical mechanism is further illustrated by the versatility of catalyst (**1**). We have found that compound (**1**) catalyses the reaction between  $\text{Fe}(\text{CO})_4\text{Bu}^t\text{NC}$  and  $\text{Bu}^t\text{NC}$  to give  $\text{Fe}(\text{CO})_3(\text{Bu}^t\text{NC})_2$ ,<sup>12</sup>  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and  $\text{Bu}^t\text{NC}$  to give  $\text{M}(\text{CO})_{6-n}(\text{Bu}^t\text{NC})_n$  ( $n = 1-3$ ),<sup>13</sup>  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Bu}^t\text{NC}$  to give  $\text{Ru}_3(\text{CO})_{11}(\text{Bu}^t\text{NC})$ ,<sup>14</sup> and  $\text{Re}_2(\text{CO})_{10}$  and  $\text{Bu}^t\text{NC}$  to give  $\text{Re}_2(\text{CO})_{10-n}(\text{Bu}^t\text{NC})_n$  ( $n = 1-2$ ).

Financial support (to M.O.A. and N.J.C.) from the University of the Witwatersrand and the C.S.I.R. is acknowledged.

(Received, 13th November 1981; Com. 1218.)

<sup>1</sup> N. J. Coville, *J. Organomet. Chem.*, 1980, **190**, C84.

<sup>2</sup> J. Halpern, *Pure Appl. Chem.*, 1979, **51**, 2171.

<sup>3</sup> A. R. Cutler and M. Rosenblum, *J. Organomet. Chem.*, 1976, **120**, 87.

<sup>4</sup> B. D. Fabian and J. A. Labinger, *J. Am. Chem. Soc.*, 1979, **101**, 2239.

<sup>5</sup> M. Rosenblum and P. S. Waterman, *J. Organomet. Chem.*, 1980, **187**, 267.

<sup>6</sup> K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *J. Organomet. Chem.*, 1963, **1**, 51.

<sup>7</sup> P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177.

<sup>8</sup> D. A. Brown, H. J. Lyons, and A. R. Manning, *Inorg. Chim. Acta*, 1970, **4**, 428.

<sup>9</sup> P. M. Treichel and D. C. Molzahn, *J. Organomet. Chem.*, 1979, **179**, 275.

<sup>10</sup> R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. Ind. (London)*, 1961, 747.

<sup>11</sup> J. Bellerby, M. J. Boylan, M. Ennis, and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1978, 185.

<sup>12</sup> M. O. Albers, N. J. Coville, T. V. Ashworth, E. Singleton, and H. Swanepoel, *J. Chem. Soc., Chem. Commun.*, 1980, 489.

<sup>13</sup> J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1972, 1246.

<sup>14</sup> M. I. Bruce, D. Schultz, R. C. Wallis, and A. D. Redhouse, *J. Organomet. Chem.*, 1979, **169**, C15.