

PRELIMINARY COMMUNICATION

THE DECARBONYLATION OF TRANSITION METAL ACYL COMPLEXES USING CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

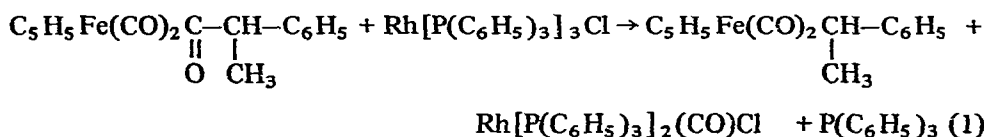
JOHN J. ALEXANDER and ANDREW WOJCICKI

The McPherson and Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received October 25th, 1968)

In the course of investigations of optically active transition metal complexes¹ we became confronted with the problem of decarbonylating $C_5H_5Fe(CO)_2[COCH(CH_3)C_6H_5]$ to the corresponding alkyl. Since both thermal and photochemical decarbonylation conditions² proved too vigorous to avoid decomposition of either the acyl dicarbonyl complex or the secondary alkyl dicarbonyl complex formed, we decided to examine reaction of $C_5H_5Fe(CO)_2[COCH(CH_3)C_6H_5]$ with $Rh[P(C_6H_5)_3]_3Cl$. Our choice of $Rh[P(C_6H_5)_3]_3Cl$ as a potential decarbonylating agent was prompted by recent disclosures^{3,4} that this complex converts aldehydes and acyl halides under mild conditions to the corresponding hydrocarbon and alkyl (aryl) halides and/or olefins, respectively, $Rh[P(C_6H_5)_3]_2(CO)Cl$ becoming the rhodium-containing product in each case.

The reaction of $C_5H_5Fe(CO)_2[COCH(CH_3)C_6H_5]^*$ with $Rh[P(C_6H_5)_3]_3Cl$ in dichloromethane at 27° for 3 h, followed by filtration to remove the precipitated $Rh[P(C_6H_5)_3]_2(CO)Cl$ (~75%) and chromatography on alumina of the filtrate, yielded the alkyl $C_5H_5Fe(CO)_2CH(CH_3)C_6H_5^*$ (54%), some $P(C_6H_5)_3$, and a trace of the unreacted acyl (eqn. 1).



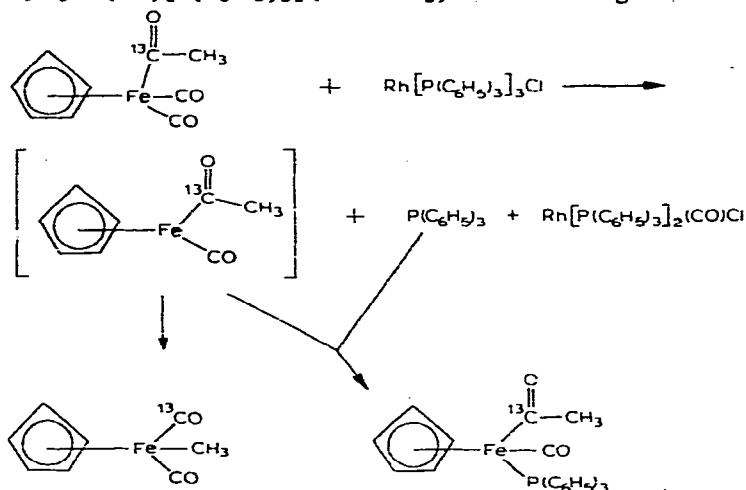
The foregoing experiment suggested further investigations designed (a) to elucidate the scope of the reaction and (b) to ascertain the source of the abstracted CO, whether from the acyl group or from a terminal position of the iron acyl complex. Reported herein are preliminary results of these studies.

The complexes $C_5H_5Fe(CO)_2(COR)$ ($R = CH_3$ and C_6H_5) react with $Rh[P(C_6H_5)_3]_3Cl$ under similar experimental conditions (CH_2Cl_2 or $CH_2Cl_2-C_6H_6$ solvent, 25–30°, 3–5 h) to afford the corresponding alkyl and aryl in 40% and 5% yields, respectively. The other isolated metal carbonyl products are $C_5H_5Fe(CO)[P(C_6H_5)_3](COR)$ ($R = CH_3$ and $C_6H_5^*$) (4% and 16%, respectively) and $Rh[P(C_6H_5)_3]_2(CO)Cl$ (88% and 100%, respectively). $C_5H_5Mo(CO)_3(COCF_3)$ yields only $C_5H_5Mo(CO)_2[P(C_6H_5)_3](COCF_3)^*$

*A new compound; satisfactory chemical analyses have been obtained.

(70%) along with $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$ (100%). No detectable reaction occurred in *ca.* 28 h between $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{COCF}_3)$ and $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$; $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{R}$ ($\text{R} = \text{CH}_3$ and $\text{CH}_2\text{C}_6\text{H}_5$) afford after 5 h virtually quantitative yields of $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$ but no iron carbonyls, suggesting rapid decomposition after abstraction of a terminal CO by the rhodium complex.

Insight into the mechanism of the above decarbonylations is obtained upon examination of the nature of the products from the reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(^{13}\text{COCH}_3)$ with $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$. The alkyl $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(^{13}\text{CO})\text{CH}_3$ and the acyl $\text{C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3](^{13}\text{COCH}_3)$ were characterized by IR spectroscopy, which also established presence of only the natural abundance of ^{13}CO in the rhodium carbonyl, $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$. The observed pattern of distribution of ^{13}CO indicates that a terminal CO is abstracted from $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(^{13}\text{COCH}_3)$; the coordinately unsaturated iron monocarbonyl then rearranges via a methyl group migration⁵ to give $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(^{13}\text{CO})\text{CH}_3$ or, alternatively, combines with $\text{P}(\text{C}_6\text{H}_5)_3$ yielding $\text{C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3](^{13}\text{COCH}_3)$. The following scheme summarizes these results:



We are currently investigating these reactions further with a view to synthesizing alkyl complexes containing transition metal – secondary and tertiary carbon bonds.

ACKNOWLEDGEMENTS

This investigation has been supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation. J.J.A. thanks The Ohio State University for a Postdoctoral Fellowship.

REFERENCES

- 1 J.J. Alexander and A. Wojcicki, in M. Cais (Ed.), *Progress in Coordination Chemistry*, Elsevier, New York, 1968, p.383–384.
- 2 R.B. King and M.B. Bisnette, *J. Organometal. Chem.*, 2 (1964) 15.
- 3 K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, 90 (1968) 99.
- 4 M.C. Baird, C.J. Nyman and G. Wilkinson, *J. Chem. Soc. A*, (1968) 348.
- 5 K. Noack and F. Calderazzo, *J. Organometal. Chem.*, 10 (1967) 101.