

## An Aldol Condensation Induced by a Transition Metal Complex

Ronald L. Bennett<sup>A</sup> and Michael I. Bruce<sup>A,B</sup>

<sup>A</sup> Department of Inorganic Chemistry, The University, Bristol BS8 1TS, England.

<sup>B</sup> Present address: Department of Physical and Inorganic Chemistry, University of Adelaide, P.O. Box 498D, Adelaide, S.A. 5001.

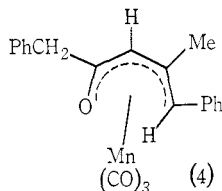
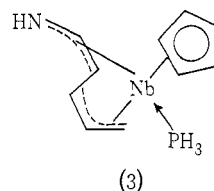
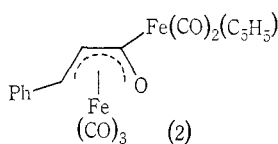
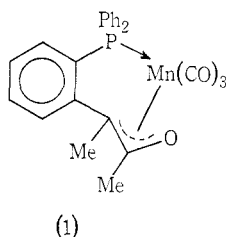
### Abstract

The reaction between benzyl methyl ketone and  $\text{MnMe}(\text{CO})_5$  affords



in which the unsaturated ligand, formed by condensation between two molecules of the ketone, acts as an acyclic heteroatom five-electron donor.

There has been some recent interest in the formation of complexes containing acyclic heteroatom systems  $\pi$ -bonded to transition metals. Reported examples of such compounds include the  $\eta^3$ -oxopropenylmanganese derivative (1),<sup>1</sup> the  $\eta^4$ -acyl complex (2),<sup>2</sup> tris( $\eta^4$ -methyl vinyl ketone)tungsten,<sup>3</sup>  $\eta^4$ -*N*-cinnamylideneaniline- $\text{Fe}(\text{CO})_3$ ,<sup>4</sup> and the unusual  $\eta^6$ -tetraphenylhexadienoniminoniobium complex (3).<sup>5</sup>



<sup>1</sup> Bennett, M. A., and Watt, R., *Chem. Commun.*, 1971, 95; Robertson, G. B., and Whimp, P. O., *Inorg. Chem.*, 1973, **12**, 1740.

<sup>2</sup> Nesmeyanov, A. N., Rybinskaya, M. I., Rybin, L. V., Kaganovich, V. S., and Petrovskii, P. V., *J. Organometal. Chem.*, 1971, **31**, 257.

<sup>3</sup> King, R. B., and Fronzaglia, A., *Inorg. Chem.*, 1966, **5**, 1837; Moriarty, R. E., Ernst, E. D., and Bau, R., *J. Chem. Soc., Chem. Commun.*, 1972, 1242.

<sup>4</sup> Cian, A. de, and Weiss, R., *Acta Crystallogr. B*, 1972, **28**, 3264.

<sup>5</sup> Kirillova, N. I., Gusev, A. I., Pasynskii, A. A., and Struchkov, Y. T., *J. Organometal. Chem.*, 1973, **63**, 311.

We describe below a further example, containing a  $\eta^5$ -enolate anion attached to manganese.

The reaction between  $\text{MnMe}(\text{CO})_5$  and benzyl methyl ketone affords a pale yellow crystalline complex (4), which from analytical and mass spectral data was assigned the formula  $(\text{C}_{18}\text{H}_{17}\text{O})\text{Mn}(\text{CO})_3$ . The infrared spectrum contained three sharp  $\nu(\text{CO})$  bands, characteristic of an  $\text{M}(\text{CO})_3$  group. The proton n.m.r. spectrum contains three sharp singlet resonances at  $\tau$  5.11, 6.24 and 8.07 (relative intensities 1:1:3) with aromatic protons as a complex multiplet at  $\tau$  2.83 corresponding to two phenyl groups. In addition, a quartet (intensity 2) occurs at  $\tau$  6.42.

These data are accommodated by a structure in which an  $\text{Mn}(\text{CO})_3$  group is attached to a ligand formed by condensation of two molecules of the ketone which acts as a five-electron donor (to satisfy the E.A.N. rule). The structure depicted satisfies the n.m.r. requirements for one methyl, two phenyl, a methylene and two methine groups. In addition, the geminal methylene protons are magnetically inequivalent, and give rise to the AB quartet observed.

The mass spectrum of complex (4) contains very weak peaks of  $m/e$  388 and 332, corresponding to  $P^+$  and  $[P-2\text{CO}]^+$ ; the base peak is the carbonyl-free  $[\text{MnC}_{18}\text{H}_{17}\text{O}]^+$  at  $m/e$  304. Loss of  $\text{C}_7\text{H}_7$  and  $\text{C}_7\text{H}_8$  from this ion gives the only other metal-containing ions, apart from  $\text{Mn}^+$ ; a metastable confirms the loss of  $\text{C}_7\text{H}_8$ . Other major ions result from breakdown of the protonated acyclic ligand (i.e. the molecular ion of the parent enone, probably formed by thermal decomposition in the source) by loss of  $\text{C}_7\text{H}_7$ , CO and  $\text{CH}_4$ . These and other ions are listed in the Experimental section.

The formation of (4) represents an example of a transition-metal induced aldol condensation. An initial reaction between  $\text{MnMe}(\text{CO})_5$  and benzyl methyl ketone, resulting in the elimination of the acidic hydrogen as methane, may produce a metal-stabilized anion which subsequently attacks a second molecule of the ketone to give the observed product. Alternatively, the  $\text{MnMe}(\text{CO})_5$  may act merely as a base to facilitate formation of the anion and subsequent condensation reaction; the resulting enolate anion then complexes with the metal.

No close analogues of (4) with  $\eta^5$ - $\text{C}_4\text{O}$  groups have been reported although the  $\text{Fe}(\text{CO})_3$  derivatives of cinnamaldehyde<sup>6</sup> and of pinocarvone<sup>7</sup> contain  $\eta^4$ - $\text{C}_3\text{O}$  donor skeletons. Further work on this and related reactions is in progress.

## Experimental

Spectra were obtained with Perkin-Elmer 257 (i.r.), Varian Associates HA 100 ( $^1\text{H}$  n.m.r., at 100 MHz) and AEI-GEC MS 902 (mass) instruments.

A mixture of  $\text{MnMe}(\text{CO})_5$  (150 mg; 0.72 mmol) and the ketone (100 mg; 0.72 mmol) was heated in refluxing heptane (30 ml) for 23 h. Chromatography of the concentrated solution on Florisil afforded a yellow material eluted with ether-hexane (1:9), and recrystallized from hexane to give yellow crystals of  $\text{Mn}(\text{CO})_3[\eta^5\text{-CHPhCMeCHC}(\text{CH}_2\text{Ph})\text{O}]$ , m.p. 78–80° (25 mg, 9%) (Found: C, 65.4; H, 4.3; Mn, 13.5.  $\text{C}_{21}\text{H}_{17}\text{MnO}_4$  requires C, 65.1; H, 4.5; Mn, 14.1%).  $\nu(\text{CO})$  (cyclohexane): 2035s, 1967ms, 1932s  $\text{cm}^{-1}$ .  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\tau$  2.83m (10H, Ph), 5.11s (1H, CMeCH), 6.24s (1H, PhCH), 6.24q (2H, PhCH<sub>2</sub>, AB quartet,  $J_{\text{AB}}$  15.0 Hz), 8.07s (3H, Me). Mass spectrum ( $m/e$ , relative intensity, assignment): 388, 0.05,  $P^+$ ; 332, 0.05 [ $P-2\text{CO}$ ] $^+$ ; 326, 12.5 [ $P-62$ ] $^+$ ; 312, 1.8 [ $P-\text{C}_6\text{H}_4$ ] $^+$ ; 304, 100 [ $P-3\text{CO}$ ] $^+ \equiv [\text{MnL}]^+$ ; 250, 3.85 [ $\text{L}+\text{H}$ ] $^+$ ; 213, 26.15

<sup>6</sup> Cian, A. de, and Weiss, R., *Acta Crystallogr. B*, 1972, **28**, 3273.

<sup>7</sup> Koerner von Gustorf, E., Grevels, F.-W., Krüger, C., Olbrich, G., Mark, F., Schulz, D., and Wagner, R., *Z. Naturforsch. B.*, 1972, **27**, 392.

$[304 - C_7H_7]^+$ ; 212, 44.3  $[304 - C_7H_8]^+$ ; 175, 4.75, —; 159, 14.2  $[(L+H) - C_7H_7]^+$ ; 146, 6.35, —; 141, 4.2  $[159 - H_2O]^+$ ; 131, 12.5  $[(L+H) - C_7H_7 - CO]^+$ ; 115, 8.65  $[(L+H) - C_7H_7CO - CH_4]^+$ ; 105, 3.4  $[(L+H) - C_7H_7CO - C_2H_2]^+$ ; 91, 75.0  $[C_7H_7]^+$ ; 77, 4.75  $[C_6H_5]^+$ ; 65, 6.35  $[C_5H_5]^+$ ; 55, 52.25,  $Mn^+$ . Metastable at  $m/e$  147.8 (calculated for  $304 \rightarrow 212$ , 147.84).

### Acknowledgment

We thank the Science Research Council for a Research Studentship (R.L.B.)

Manuscript received 20 December 1974