Inorganica Chimica Acta, *88* (1984) L5–L6

Alkyne Derivatives of $[CoMn(CO)_9]$

P. J. MANNING and L. K. PETERSON

Department of Chemistry, Simon Fraser University, Burnaby, B.C., Canada V5A 1S6

Received April 9, 1984

Alkyne-bridged dinuclear transition metal complexes usually show the alkyne ligand orthogonal to the metal–metal bond vector [1], thus forming tetrahedrane C_2M_2 core structures. In a less common type of structure, the alkyne and metal–metal vectors are parallel [2]. Hoffmann *et al.* [1a] have studied the theoretical aspects of bonding in both forms. In this note, we report the synthesis and spectroscopic characterization of several $[(RC_2R')CoMn(CO)_7]$ complexes, obtained via the reaction of $[CoMn(CO)_9]$ [3] with the internal alkynes $C_2H_5C{\equiv}CC_2H_5$, $C_2H_5C{\equiv}CCH_3$, $CH_3C{\equiv}CC_6H_5$ and $C_6H_5C{\equiv}CC_6H_5$.

The soluble $[(RC_2R')CoMn(CO)_7]$ complexes were readily prepared by refluxing a hexane solution of $[CoMn(CO)_9]$ containing a slight excess of the alkyne [1]. The facility of CO substitution in $[CoMn(CO)_9]$ is comparable to that in $[Co_2(CO)_8]$ [4], for which an extensive alkyne chemistry is known [4, 5]. In contrast, however, the dinuclear species $[Mn_2(CO)_{10}]$ [6] and $[Re_2(CO)_{10}]$ [7] apparently do not afford simple alkyne derivatives. Extended heating of solutions of $[(RC_2R')CoMn(CO)_7]$ gave rise to ν(CO) bands corresponding to $[(RC_2R')Co_2(CO)_6]$ derivatives, formed at the expense of $[(RC_2R')CoMn(CO)_7]$. The latter products were difficult to obtain pure because of facile decomposition into $[(RC_2R')Co_2(CO)_6]$ and other unidentified products. By using silica-gel chromatography, satisfactory samples of $[(RC_2R')CoMn(CO)_7]$ (**I**, $R = R' = C_2H_5$; **II**, $R = C_2H_5$, $R' = CH_3$; **III**, $R = CH_3$, $R' = C_6H_5$; **IV**, $R = R' = C_6H_5$) were obtained and characterized as described below.*

The compounds **I**–**IV** are low melting, orange, waxy solids or viscous oils. They are stable at ambient temperature in non-polar, hydrocarbon solvents, but decompose in halogenated solvents, and in polar solvents. In the latter case, one of the main products is $[(RC_2R')Co_2(CO)_6]$. The mass spectra of **I**–**IV** showed a weak molecular ion in all cases, together with fragments corresponding to the sequential loss of seven CO groups. The base peak for **I**, **II** and **IV** was $[CoMn(RC_2R')]^+$, while for **III** the strongest signal corresponded to $[Co(C_6H_5C_2CH_3)]^+$. The $[Mn(RC_2R')]^+$ ion was notably absent in all cases except for its weak appearance in the mass spectrum of **I**.

The infrared spectra (ν(CO) region) of **I**–**IV** showed a characteristic pattern of six carbonyl absorptions, reflecting the low symmetry of the essentially $C_1Co(CO)_3$ and $Mn(CO)_4$ metallocarbonyl units.

The ^1H nmr spectra of compounds **I**–**IV** were consistent with the given formulations. In **I** and **II**, two broad resonances were observed for the methylene protons. These two signals collapsed to an AB quartet upon decoupling the CH_3 protons. The inequivalence of the methylenic protons is consistent for a tetrahedrane $[CoMnC_2]$ core structure which must also be rigid on the nmr time scale at room temperature. At higher temperatures, spectral resolution was lost due to formation of paramagnetic species.

The ^{13}C nmr spectra of **I**–**IV** showed two broad absorptions for the carbonyl resonances at room temperature. These signals became progressively sharper as the temperature was lowered. The lower field absorption, assigned to the $Mn(CO)_4$ moiety by comparison with literature data [8], was ultimately resolved in several signals – three for compounds **I** and **IV**, and four for compounds **II** and **III**. The higher field signal, due to the $Co(CO)_3$ moiety, sharpened to a singlet on cooling in all cases, but was not resolved further even at 213 K. Thus, carbonyl exchange at the pseudo five-coordinate cobalt atom is facile even at low temperature. It seems likely, by comparison with the published studies of CO exchange in $[Co_2(CO)_5(PR_3)(alkyne)]$ complexes [9] that the carbonyl exchanges

---

*Typically, syntheses of compounds **I**–**IV** were done on a 0.5–1.0 millimolar scale, using Schlenk apparatus and a dry, de-oxygenated N_2 atmosphere. The progress of reactions was followed by monitoring the decay of the 2115 cm^{-1} band (ν(CO) of $CoMn(CO)_9$) and the growth of bands at 2082–6 and 1960–2 cm^{-1} due to $[(RC_2R')CoMn(CO)_7]$. The following spectroscopic data were recorded: $[(C_2H_5C_2C_2H_5)CoMn(CO)_7]$, **I**, P 392; ν(CO) 2082 m, 2034 vs, 2011 vs, 2005 vs, 1981 m, 1960 s; ^{13}C nmr, 92.6 (alkyne C's), 223.8, 221.9, 215.2, 203.4 (carbonyl groups, at 213 K). $[(C_2H_5C_2CH_3)CoMn(CO)_7]$, **II**, P 378; ν(CO) 2083 m, 2035 vs, 2013 vs, 2006 s, 1982 m, 1961 m; ^{13}C 92.0, 89.1 (alkyne C's), 223.5, 221.7, 221.4, 214.6, 202.7 (carbonyl groups, at 213 K). $[(C_6H_5C_2CH_3)CoMn(CO)_7]$ **III**, P 426; ν(CO) 2085 m, 2040 vs, 2016 vs, 2011 vs, 1987 m, 1962 s; ^{13}C 88.6, 87.5 (alkyne C's), 223.3, 221.5, 220.4, 214.1, 202.2 (carbonyl groups, at 213 K). $[(C_6H_5C_2C_6H_5)CoMn(CO)_7]$, **IV**, P 488; ν(CO) 2086 m, 2043 vs, 2017 vs, 2014 vs, 1994 w, 1961 m; ^{13}C 90.7 (alkyne C s), 222.7, 219.6, 214.2, 201.7 (carbonyl groups, at 213 K).

0020-1693/84/$3.00

described above for $[(RC_2R')CoMn(CO)_7]$ systems are also intramolecular and localized at the individual metal centers. Thus, the observed signal broadening of the ^{13}C signals at temperatures above 213 K may be attributed to quadrupolar coupling with the Mn ($I = 5/2$) and Co ($I = 7/2$) nuclei, rather than to exchange between the two different metal centers. This conclusion was corroborated by observing the ^{17}O nmr spectrum of $[(C_2H_5C_2C_2H_5)CoMn(CO)_7]$ (I) in hexane. The spectrum consisted of a sharp signal for the $Co(CO)_3$ (rapid exchange), and a broad signal, at slightly lower field, for the $Mn(CO)_4$ group. For the latter group, the ^{17}O signal broadening is evidently due to the relatively slower rate of exchange of the carbonyl groups. Both $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]$ have been reported to give sharp ^{17}O nmr signals, indicating that quadrupolar broadening effects are minimal at these remote nmr-active centers [10].

Acknowledgements

The financial support of this research, by the Natural Sciences and Engineering Research Council of Canada, is acknowledged.

References

1 (a) D. M. Hoffman, R. Hoffmann and C. R. Fisel, *J. Am. Chem. Soc.*, *104*, 3858 (1982).
(b) W. I. Bailey, M. H. Chisholm, F. A. Cotton and L. A. Rankel, *ibid.*, *100*, 5764 (1978).
(c) F. A. Cotton, J. D. Jamerson and B. R. Stults, *ibid.*, *98*, 1774 (1976).
(d) W. G. Sly, *ibid.*, *81*, 18 (1959).
(e) P. H. Bird, A. R. Fraser and D. N. Hall, *Inorg. Chem.*, *16*, 1923 (1977).
(f) N. A. Bailey, M. R. Churchill, R. Hunt, R. Mason and G. Wilkinson, *Proc. Chem. Soc. (London)*, 401 (1964).
2 For a listing, see Ref. 1(a).
3 K. K. Joshi and P. L. Pauson, *Z. Naturforsch.*, *176*, 565 (1962).
4 R. S. Dickson and P. J. Fraser, *Adv. Organometal. Chem.*, *12*, 323 (1974).
5 (a) R. D. W. Kemmitt and D. R. Russell, in ' Comprehensive Organometallic Chemistry', G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds., Vol. 5, Pergamon Press, Oxford (1982).
(b) M. R. Churchill and R. Mason, *Adv. Organometal. Chem.*, *5*, 93 (1967).
6 (a) R. B. King and C. A. Harmon, *Inorg. Chem.*, *15*, 880 (1976).
(b) W. Hubel, in 'Organic Syntheses via Metal Carbonyls', I. Wender and P. Pino, Eds., Interscience, New York, N.Y. (1968).
(c) F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, *3*, 227 (1968).
7 M. J. Mays, D. W. Prest and P. R. Raithby, *J. Chem. Soc. Dalton Trans.*, 771 (1981).
8 B. E. Mann and B. F. Taylor, in '^{13}C NMR Data for Organometallic Compounds', Academic Press, London (1981).
9 S. Aime, L. Milone, R. Rossetti and P. L. Stanghellini, *Inorg. Chim. Acta*, *22*, 135 (1977).
10 J. P. Hickey, J. R. Wilkinson and L. E. Todd, *J. Organometal. Chem.*, *179*, 159 (1979).