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BIIMIDAZOLATE- AND BIBENZIMIDAZOLATE-BRIDGED BINUCLEAR SUBSTITUTED MANGANESE(I) CARBONYL COMPLEXES

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Summary

Novel binuclear substituted manganese(I) carbonyls $[Mn(CO)_{4-n}L_n]_2(\mu\text{-N-N})_2$ ($n = 1$, $(N\text{-}N)_2$ = biimidazolate, L = PBu^n_3; $(N\text{-}N)_2$ = bibenzimidazolate, L = $P(OMe)_3$, $P(OPh)_3$, PPh_3, PEt_3 or PBu^n_3, as well as $n = 2$; $(N\text{-}N)_2$ = biimidazolate, or bibenzimidazolate, L = PBu^n_3, PEt_3 or $P(OMe)_3$) are described, in which the anions $(N\text{-}N)_2$ act as tetradentate bridging-groups. They were prepared by treating $[Mn(CO)_4(\mu\text{-Br})]_2$ with thallium or potassium salts of 2,2'-biimidazole or 2,2'-bibenzimidazole and subsequent displacement of CO by L. The structures of the complexes are discussed.

Introduction

The small number of hitherto-known neutral binuclear substituted manganese carbonyls in which both metal atoms are linked via a double bridge belong to the following three types: a) $[Mn(CO)_{4-n}L_n(\mu\text{-X})]_2$ (X = Cl; L = THF or CH_3CN; $n = 1$) [1] (X = SR or SeR; L = PPh_3; $n = 1$) [2]; b) $[Mn(CO)_3(\mu\text{-XY})]_2$ (XY = SN, SO or SP) [3]; and c) $[Mn(CO)_3(\mu\text{-Br})]_2(\mu\text{-dam})$ [4]; in which the two $Mn(CO)_3$ moieties are triple-bridged through two Br and one dam [(diphenylarsine)methane] groups. Generally, abstraction of further carbonyl groups by other ligands does not take place because competitive processes cause cleavage of the bridges, leading to the formation of mononuclear compounds [3b]. Further substitution in binuclear Mn^I carbonyls can, however, be achieved by the use of special ligands such as the tetradentate anions biimidazolate, $[BiIm]^{2-}$, or bibenzimidazolate, $[BiBzIm]^{2-}$, which lead to much more stable bridging systems, resistant to cleavage, as described in the present paper. Binuclear compounds of the types $[Mn(CO)_{4-n}L_n]_2(\mu\text{-N-N})_2$ ($n = 1$ or 2; $(N\text{-}N)_2$ = $BiIm^{2-}$ or $BiBzIm^{2-}$; L = monodentate P-donor ligands) have been prepared by the abstraction of CO groups from $[Mn(CO)_4]_2(\mu\text{-N-N})_2$ by ligands L.

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Results and discussion

a) Tetracarbonyl complexes

The reaction (1 : 1, room temperature) between dichloromethane solutions of $[Mn(CO)_4(\mu\text{-Br})]_2$ and potassium or thallium salts of $BiIm^{2-}$ or $BiBzIm^{2-}$, according to eq. 1 leads to yellow solutions which yield crystals of $[Mn(CO)_4]_2$

$$[Mn(CO)_4(\mu\text{-Br})]_2 + M_2(N\text{-}N)_2 \xrightarrow{-2\,MBr} [Mn(CO)_4]_2(\mu\text{-}N\text{-}N)_2 \qquad M = K, Tl \qquad (1)$$

(μ-BiBzIm) (I), or, for $(\mu\text{-}N\text{-}N)_2 = BiIm^{2-}$, mixtures of binuclear tetra- and tricarbonyls. Both processes can be monitored by observing the ν(CO) stretching region of the IR spectra, in which the four absorption bands of the starting complex (2095w, 2040vs, 2010m, 1975s) are gradually replaced by another four characteristics of complex I (ν(CO) in CH_2Cl_2: 2100w, 2025vs, 2000m and 1975s cm^{-1}) or by a similar pattern which, however, shows additional weak bands attributable to contamination by tricarbonyls (for $(\mu\text{-}N\text{-}N)_2 = BiIm^{2-}$) (see Experimental).

b) Tricarbonyl complexes

Refluxing solutions of the tetracarbonyls in $CHCl_3$, THF or Me_2CO (obtained in situ according to eq. 1) react (1 : 2) with P-donor ligands to give tricarbonyl derivatives (eq. 2)

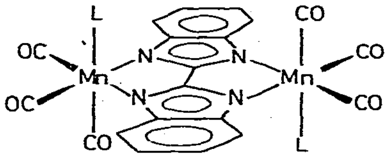
$$[Mn(CO)_4]_2(\mu\text{-}N\text{-}N)_2 + 2\,L \xrightarrow{-2CO} [Mn(CO)_3L]_2(\mu\text{-}N\text{-}N)_2 \qquad (2)$$

$(N\text{-}N)_2 = (BiBzIm)^{2-}$; $L = P(OMe)_3$(II), $P(OPh)_3$(III), PPh_3(IV),
PEt_3(V), PBu^n_3(VI)

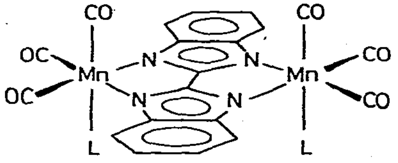
$(N\text{-}N)_2 = (BiIm)^{2-}$; $L = PBu^n_3$(VII)

The reaction time varies from 0.5 to 2 h, being shorter the more basic and higher-boiling is the solvent and the more π-acidic is the ligand L. Moreover, only complex VII could be isolated in pure state, since for $(N\text{-}N)_2 = BiIm^{2-}$ the dicarbonyl derivatives are formed simultaneously (IR spectra) even when exact stoichiometric amounts of L are used.

Three absorption bands due to ν(CO) are found in the IR spectra of complexes II—VII, though the intensity pattern excludes the presence of *mer*-tricarbonyls. The three observed IR-active absorption bands ($A_u + 2B_u$) are as expected for *fac*-tricarbonyls of structure Ia (C_{2h}), therefore, the other possible configuration Ib (C_{2v}), for which five IR-active bands ($2A_1 + 2B_1 + B_2$) are expected, can be ruled out.



(Ia)



(Ib)

c) Dicarbonyl complexes

Addition of an excess of the P-donor ligands to filtered solutions (in Me_2CO

TABLE I

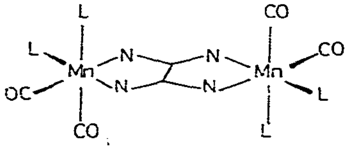
ANALYTICAL AND IR ν(CO) DATA FOR COMPLEXES I—XIII

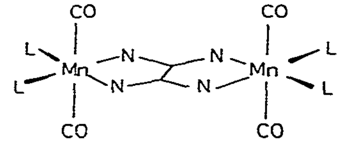
	Complexes	Analyses: Found(calcd)			ν(CO) (cm^{-1}) (CH_2Cl_2)	Mol. weight Found(calcd)	M.p. (°C)
		C	H	N			
I	$[\mathrm{Mn(CO)_4}]_2(\mu\text{-BiBzIm})$	45.16 (46.67)	1.53 (1.42)	9.39 [a] (9.89)	2100w, 2025vs, 2000s, 1957s	612 (566.2)	70 [b]
II	$[\mathrm{Mn(CO)_3P(OMe)_3}]_2(\mu\text{-BiBzIm})$	42.20 (41.18)	7.96 (7.38)	3.87 (3.45)	2045s, 1970s 1930s	710 (758.3)	147—149
III	$[\mathrm{Mn(CO)_3P(OPh)_3}]_2(\mu\text{-BiBzIm})$	58.58 (59.51)	3.67 (3.39)	4.18 (4.95)	2040s, 1970s, 1930s	1023 (1130.7)	155—157
IV	$[\mathrm{Mn(CO)_3PPh_3}]_2(\mu\text{-BiBzIm})$	65.25 (65.04)	2.79 (3.70)	5.49 (5.41)	2020s, 1945s, 1910s	992 (1033.9)	150—152
V	$[\mathrm{Mn(CO)_3PEt_3}]_2(\mu\text{-BiBzIm})$	51.86 (51.49)	5.39 (5.13)	7.4 (7.5)	2020s, 1935s, 1905s	612 (746.5)	178—180
VI	$[\mathrm{Mn(CO)_3PBu^n_3}]_2(\mu\text{-BiBzIm})$	57.10 (57.39)	6.89 (7.44)	5.90 (6.09)	2010s, 1935s, 1905s	900 (920.8)	163—165
VII	$[\mathrm{Mn(CO)_3PBu^n_3}]_2(\mu\text{-BiIm})$	53.49 (53.07)	7.69 (7.17)	7.26 (6.87)	2020s, 1935s, 1900s	720 (814.6)	98—100
VIII	$[\mathrm{Mn(CO)_2\{P(OMe)_3\}_2}]_2(\mu\text{-BiBzIm})$	37.83 (37.91)	4.63 (4.66)	5.68 (5.89)	1945s, 1870s	895 (950.4)	250 [b]
IX	$[\mathrm{Mn(CO)_2(PEt_3)_2}]_2(\mu\text{-BiBzIm})$	54.45 (54.43)	7.48 (7.39)	6.06 (6.07)	1910s, 1830s	851 (926.8)	223—225 [b]
X	$[\mathrm{Mn(CO)_2(PBu^n_3)_2}]_2(\mu\text{-BiBzIm})$	63.23 (62.78)	9.36 (9.18)	4.35 (4.43)	1910s, 1830s	1265 (1263)	190—192
XI	$[\mathrm{Mn(CO)_2\{P(OMe)_3\}_2}]_2(\mu\text{-BiIm})$	31.34 (31.07)	4.76 (4.74)	6.78 (6.58)	1945s, 1870s	840 (850.3)	210 [b]
XII	$[\mathrm{Mn(CO)_2(PBu^n_3)_2}]_2(\mu\text{-BiIm})$	58.80 (59.88)	9.57 (9.70)	5.07 (4.82)	1920s, 1840s	991 (1163.3)	165—167
XIII	$[\mathrm{Mn(CO)_2(PEt_3)_2}]_2(\mu\text{-BiIm})$	48.29 (49.39)	7.67 (7.80)	6.67 (6.78)	1905s, 1825s	776 (826.7)	206—208

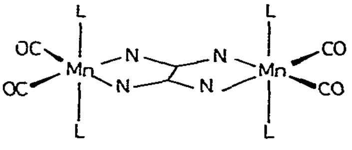
[a] See Experimental. [b] Decomposes.

or THF) of the tetracarbonyls obtained according to eq. 1, followed by 10—60 min refluxing gives solutions whose IR pattern shows the presence of dicarbonyls. These can be isolated by evaporation (complexes VIII—XIII, Table 1). For L = $P(OPh)_3$ or PPh_3 the step tricarbonyl—dicarbonyl does not proceed to completion, and prolonged treatment leads to decomposition and precipitation of insoluble products whose IR spectra do not show any bands assignable to ν(CO), and which were therefore not further studied.

Of the ten stereoisomers which are possible for complexes of the general formula $[Mn(CO)_2L_2]_2(\mu\text{-N-N})_2$, only three should show the two ν(CO) IR-active absorptions which appear in the spectra of complexes VIII—XIII (Table 1).


IIa (C_i)


IIb (D_{2h})


IIc (D_{2h})

The assignment of structure IIc is based on the following reasoning:
a) The ^1H NMR spectra of complexes VIII and XI (L = $P(OMe)_3$) show resonances arising from the protons of the bridging ligands $BiIm^{2-}$ and $BiBzIm^{2-}$, as a singlet for the former, and as a doublet of multiplets (A_2B_2 system) for the latter; the patterns are similar to those of the free ligands though somewhat shifted [5,6,7]. More significantly, both spectra show triplets for the CH_3 groups of the ligand L, pointing to virtual coupling to two *trans* phosphorus atoms.
b) As is known [8,9], the nitrogen atoms of the ligand ($BiIm^{2-}$ or $BiBzIm^{2-}$) tend to labilize *cis* CO groups, which means that the CO group *trans* to L in Ia should be the most labile. Substitution reactions should therefore result in abstraction of this group, and the resulting dicarbonyl should have configuration IIc.

Table 1 lists the analytical data for all the complexes isolated along with their ν(CO) stretching vibrations and molecular weights. The latter were determined osmometrically in chloroform, and the values confirm the binuclear character of the complexes. The IR spectra (Nujol mulls) show absorptions characteristic of the tetradentate anions $BiIm^{2-}$ and $BiBzIm^{2-}$ [10]. The ^1H NMR spectra of the dicarbonyls show the expected resonances from the protons of the phosphorus ligands L, though no further information could be obtained from these spectra, except for the dicarbonyls with L = $P(OMe)_3$ (see above).

Experimental

C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. Molecular weights were determined in chloroform solutions with a Hitachi-Perkin-Elmer model 115 osmometer. The IR spectra in the ν(CO) stretching region were recorded on a Perkin Elmer 577 spectrophotometer in dichloromethane or hexane solutions between NaCl discs, or in Nujol mulls between polyethylene sheets. The polystyrene absorption at 1601.8 cm^{-1} was used as a standard in every case. The ^1H NMR spectra were recorded in $CDCl_3$ solutions on a Varian T-60 spectrophotometer at 60 MHz using $SiMe_4$ as internal standard.

All reactions were carried out under nitrogen and the solvents were dried before use. $[Mn(CO)_4(\mu\text{-}Br)]_2$ was obtained by refluxing $Mn(CO)_5Br$ in cyclohexane [11]. $H_2BiBzIm$, H_2BiIm and its thallium salts were prepared as described elsewhere [7,10]. The ligands were used as purchased.

Preparation of the complexes

$[Mn(CO)_4]_2(\mu\text{-}BiBzIm)$ (I)

A mixture of $[Mn(CO)_4(\mu\text{-}Br)]_2$ (0.346 g; 0.5 mmol) and $Tl_2BiBzIm$ (0.32 g; 0.5 mmol) in 30 ml of CH_2Cl_2 was stirred for 3 h at room temperature. The TlBr formed was filtered off, the filtrate was partially evaporated under reduced pressure, and diethyl ether was added to give a yellow solid (Yield: 0.212 g; 75%; the C, H and N analyses gave values which were lower than the calculated ones, because of the presence of CH_2Cl_2, which could not be completely eliminated).

Reaction of $[Mn(CO)_4(\mu\text{-}Br)]_2$ with Tl_2BiIm

A mixture of $[Mn(CO)_4(\mu\text{-}Br)]_2$ (0.246 g; 0.5 mmol) and Tl_2BiIm (0.27 g; 0.5 mmol) in 30 ml of CH_2Cl_2 was stirred at room temperature, the reaction being monitored by scans of the $\nu(CO)$ stretching region. (After 10 min absorptions due to a tetracarbonyl complex were observed at 2100w, 2040vs, 2010s and 1975s cm^{-1} along with those assignable to a tricarbonyl species at 2020s(sh) and 1920(br) cm^{-1}.) After filtering off the TlBr, addition of hexane and partial evaporation under reduced pressure gave a yellow solid which according to its C, H and N analysis was a mixture of the tri- and tetracarbonyls.

$[Mn(CO)_3L]_2(\mu\text{-}BiBzIm)$ ($L = P(OMe)_3$ (II), $P(OPh)_3$ (III), PPh_3 (IV), PEt_3 (V) or PBu^n_3 (VI))

An equimolecular mixture of $[Mn(CO)_4(\mu\text{-}Br)]_2$ and $Tl_2BiBzIm$ (0.5 mmol) in 50 ml of $CHCl_3$ was refluxed for 1 h. The suspension was cooled to room temperature and 1 mmol of the relevant ligand was added with stirring, and the mixture was then stirred for 30 min at room temperature (II and III), refluxed for 30 min (IV), or refluxed for 60 min (V and VI). The TlBr was filtered off, and the $HCCl_3$ was partially evaporated under reduced pressure. Addition of hexane (under stirring) led to the precipitation of the pale yellow complexes. Yields: II, 85%; III, 85%; IV, 35%; V, 54%; VI, 38%.

$[Mn(CO)_3L]_2(\mu\text{-}BiIm)$ ($L = PBu^n_3$ (VIII))

A mixture of $[Mn(CO)_4(\mu\text{-}Br)]_2$ (0.246 g; 0.5 mmol) and K_2BiIm (obtained by stirring 0.5 mmol of H_2BiIm with 1 mmol of KOH for 2 h at room temperature) in 50 ml of THF was refluxed for 30 min. After cooling to room temperature 1 mmol of PBu^n_3 was added and stirring was continued for 5 min. The suspension was filtered through Celite and the THF was removed in vacuo. The yellow residue was extracted with 20 ml of hexane, and the extract was cooled to 0°C to give the yellow needles of VII.
Yield: 0.123 g, 30%.

$L = P(OMe)_3$, PEt_3, $P(OPh)_3$ or PPh_3. The corresponding complexes could not be isolated. The IR spectra of their solutions in the ν(CO) stretching region show absorptions corresponding to a mixture of tri- and dicarbonyls.

$[Mn(CO)_2L_2]_2(\mu\text{-}BiBzIm)$ ($L = P(OMe)_3$ (VIII); PEt_3 (IX) or PBu^n_3 (X))

An equimolecular mixture of $[Mn(CO)_4(\mu\text{-}Br)]_2$ and $Tl_2BiBzIm$ (0.25 mmol) in 50 ml of THF was refluxed for 30 min and an excess of the respective ligand L (ca. 2 mmol) was added. Evolution of CO occurred, and the reaction was continued until the IR spectra in the ν(CO) stretching region showed the two absorptions characteristic of a dicarbonyl ((VIII): 10 min; (IX, X): 1 h). THF was removed in vacuo and the residue was extracted with CH_2Cl_2. After the TlBr had been filtered off, the yellow complexes were isolated by addition of hexane and partial evaporation under reduced pressure.
Yields: 70—80%.
^{1}H NMR: δ 7.8(m), 7.1(m) (BiBzIm); VIII: δ 3.4(t) (^3J(P—H) 11 Hz); IX: δ 1.2(m) (CH_3—CH_2); X: δ 0.95(m) (CH_3), 1.3(m) $(CH_2)_n$.

$[Mn(CO)_2L_2]_2(\mu\text{-}BiIm)$ ($L = P(OMe)_3$ (XI); PBu^n_3 (XII) or PEt_3 (XIII))

To a suspension of 0.25 mmol of K_2BiIm in 30 ml of acetone (obtained by stirring H_2BiIm with KOH for 2 h at room temperature) was added $[Mn(CO)_4(\mu\text{-}Br)]_2$ (0.123 g; 0.25 mmol). After 30 min refluxing an excess of the ligand (L = PBu^n_3 or PEt_3) (ca. 1.5 mmol) was added. Evolution of CO occurred, and refluxing was continued until the IR spectra in the ν(CO) stretching region showed the two absorptions characteristic of a dicarbonyl (ca. 1 h). The solution was filtered through Celite and concentrated under reduced pressure to ca. 5 ml. Yellow microcrystalline solids were obtained by addition of hexane and cooling to 0°C.
Yields: XII, 38%; XIII, 55%.
^{1}H NMR: XII: δ 0.95(m) $[CH_3]$; 1.3(m) $[CH_2]_n$; 6.9(s) [BiIm]; XIII: δ 1.2(m) $[CH_3CH_2]$; 7.0(s) [BiIm].

Complex XI was obtained by a similar reaction (L = $P(OMe)_3$; 30 min refluxing in THF) and isolated by evaporating to dryness, washing the residue with hexane (2 × 10 ml) and extraction with CH_2Cl_2. Partial evaporation under reduced pressure gave a white solid (30 mg) which could not be identified (m.p. > 260°C (dec); ν(CO) in CH_2Cl_2 1945s, 1870s cm^{-1}. Analysis: C, 34.59; N, 10.69; H, 4.70%). Further evaporation of the filtrate and cooling to 0°C gave the pale-yellow complex XI.
Yield: 0.13 g, 31%.
^{1}H NMR: δ 3.4(t) (^3J(P—H) = 11 Hz); 7.0(s) [BiIm].

References

1 a) M.C. Van der Veer and J.M. Burlitch, J. Organometal. Chem., 197 (1980) 357; b) J.G. Dunn and D.A. Edwards, J. Organometal. Chem., 27 (1971) 73.
2 E.W. Abel, A.M. Atkins, B.C. Crosse and G.V. Hutson, J. Chem. Soc. (A), (1968) 687.
3 a) S.R. Finnimore, R. Goddard, S.D. Killops, S.A.R. Knox and P. Woodward, J. Chem. Soc. Dalton, (1978) 1247; b) E.W. Abel and J.D.H. Towle, J. Organometal. Chem., 12 (1976) 253; c) E.W. Abel and M.D. Dunster, J. Chem. Soc. Dalton, (1973) 98; d) K. Tanaka, Y. Miya-Uchi and T. Tanaka, Inorg. Chem., 14 (1975) 1548; e) M. Savignac, P. Cadiot and F. Mathey, Inorg. Chim. Acta Letters, 45 (1980) L43.

4 R. Colton and M.J. McCormick, Aust. J. Chem., 29 (1976) 1657.
5 G.S. Reddy, L. Mandell and J.H. Goldstein, J. Chem. Soc., (1963) 1414.
6 P.S. Black and M.L. Heffernan, Aust. J. Chem., 15 (1962) 862.
7 B.F. Fieselmann, D.N. Hendrickson and G.D. Stucky, Inorg. Chem., 17 (1978) 2078.
8 a) G.R. Dobson, Acc. Chem. Res., 8 (1976) 300; b) J.D. Atwood and T.L. Brown, J. Amer. Chem. Soc., 98 (1976) 3160; c) D.L. Lichtenberger and T.L. Brown, J. Amer. Chem. Soc., 100 (1978) 366.
9 R. Usón, V. Riera, J. Gimeno and M. Laguna, Transition Met. Chem., 2 (1977) 123.
10 R. Usón, J. Gimeno, J. Forniés and F. Martínez, Inorg. Chim. Acta, in press.
11 E.W. Abel and G. Wilkinson, J. Chem. Soc., (1959) 1501.