994. *Substituted Group VI Carbonyls. Part VI.*[1] *Derivatives containing 2,6-Dimethylpyrazine and 2,2′,2″-Terpyridyl*

By M. C. GANORKAR and M. H. B. STIDDARD

The ligand 2,6-dimethylpyrazine (2,6-DMP) reacts with the hexacarbonyls of chromium, molybdenum, and tungsten to yield, respectively, complexes of the type $M(CO)_5(2,6\text{-DMP})$ and $M(CO)_3(2,6\text{-DMP})_3$. Use of the terdentate ligand 2,2′,2″-terpyridyl (Terpy) leads to products of two types: (i) that in which the ligand behaves as a bidentate chelate, *viz.*, $M(CO)_4(\text{Terpy})$ ($M = Cr$, Mo, and W); (ii) that in which the ligand displaces three carbonyl groups, *viz.*, $Mo(CO)_3(\text{Terpy})$.

PYRIDINE is known to replace up to three carbonyl groups in the hexacarbonyls of Group VI metals,[2] but the only reported complexes containing a pyrazine nucleus are the tetracarbonylbis-2-methylpyrazine derivatives of chromium and molybdenum.[3] Since such ligands may have the capacity to co-ordinate to two metal atoms, a study of the reactions of 2,6-dimethylpyrazine (2,6-DMP) with the hexacarbonyls of chromium, molybdenum, and tungsten was undertken. On heating one equivalent of the ligand with the hexacarbonyls in an evacuated tube, the monosubstituted derivatives $M(CO)_5(2,6\text{-DMP})$ were formed. They are stable in air, diamagnetic in the solid state, and non-electrolytes in nitrobenzene (see Table). Attempts to prepare the bis-substituted carbonyls were unsuccessful; reactions under a variety of conditions, together with the reaction of tetracarbonylnorbornadienemolybdenum failed to yield the expected products, although some spectroscopic evidence for their formation was obtained. Reaction of 2,6-dimethylpyrazine with the compounds $Mo(CO)_3$(mesitylene) and $W(CO)_3$(mesitylene) led to air-sensitive products of the type $M(CO)_3(2,6\text{-DMP})_3$ (see Table). No products of reaction of the ligand with tricarbonylmesitylenechromium could be isolated.

---

[1] Part V, C. D. Cook, R. S. Nyholm, and M. L. Tobe, *J.*, 1965, 4194.

[2] W. Hieber and F. Muhlbauer, *Z. anorg. Chem.*, 1935, **221**, 337; H. Behrens and W. Klek, *ibid.*, 1957, **292**, 151; E. W. Abel, M. A. Bennett, and G. Wilkinson, *J.*, 1959, 2323; W. Strohmeier, Kl. Gerlach, and G. Matthias, *Z. Naturforsch.*, 1962, **15**b, 621; W. Strohmeier and Kl. Gerlach, *ibid.*, 1960, **15**b, 413.

[3] A. Luttringhaus and W. Kullick, *Tetrahedron Letters*, 1959, No. 10, 13.

Properties of complexes

			M by osmometry			I.r. active C–O stretching frequencies
Compound	Colour	Λ_m [a]	Found	Concn. ($\text{M} \times 10^2$)	Calc.	(cm.$^{-1}$ in chloroform)
$Cr(CO)_5(2,6\text{-DMP})$ ...	Yellow	0·07	292 [b]	2·0	300	2080m, 1990m, 1940s, 1908sh
$Mo(CO)_5(2,6\text{-DMP})$ ...	Yellow	0·08	341 [b]	1·6	344	2084m, 1990m, 1941s, 1908sh
$W(CO)_5(2,6\text{-DMP})$ ...	Yellow	0·09	444 [b]	2·3	432	2079m, 1985m, 1936s, 1906sh
$Mo(CO)_3(2,6\text{-DMP})_3$ ...	Red	0·14		[e]		1898m, 1800m, 1775s [f]
$W(CO)_3(2,6\text{-DMP})_3$ ...	Red	0·15		[e]		1898m, 1795m, 1775s [f]
$Cr(CO)_4(\text{Terpy})$	Deep red	[d]		[e]		2008m, 1895vs, 1880sh, 1825s
$Mo(CO)_4(\text{Terpy})$	Deep red	0·43	461 [c]	0·58	441	2008m, 1902vs, 1880sh, 1830s
$W(CO)_4(\text{Terpy})$	Deep red	[e]	503 [c]	0·45	529	2006m, 1898vs, 1880sh, 1828s
$Mo(CO)_3(\text{Terpy})$	Deep maroon	[c]		[e]		1898m, 1792m, 1770s [f]
$Mn(CO)_3(\text{Terpy})Br$ ...	Orange	0·14	441 [c]	0·92	452	2040s, 1950s, 1920s

[a] (Ohm^{-1} cm.^{2}), of 10^{-3}M solutions in $PhNO_2$. [b] In benzene. [c] In chloroform. [d] Solution unstable. [e] Insufficiently soluble. [f] In Nujol.

The infrared (i.r.) spectra of the compounds in the C–O stretching region are recorded in the Table. The spectra of the monosubstituted derivatives are very similar to those of the analogous pyridine and cyclohexylamine complexes,[4] suggesting that 2,6-dimethylpyrazine has little tendency to act as a π-acceptor. In the spectra of the tris-complexes, the appearance of three bands suggests that the carbonyl groups occupy the unusual *trans*-positions of the C_{2v} molecule. In similar tricarbonyl complexes, it is much more usual for the ligands to occupy mutually *cis* positions.

Behrens and Anders[5] prepared the compounds $M(\text{Terpy})_2$ (M = Cr, Mo, and W; Terpy = 2,2′,2″-terpyridyl) by direct reaction of the carbonyls. We have also studied the reaction of the ligand with the hexacarbonyls under different conditions and, while confirming the formation of complexes without carbonyl groups, have isolated also in a pure state other terpyridyl-containing complexes. Ultraviolet irradiation of a solution of the terpyridyl and hexacarbonylchromium in isopentane produces an unstable dark red compound, whose i.r. spectrum in the C–O stretching region is identical with that of the compound $Cr(CO)_4(\text{Bipy})$,[6] (Bipy = 2,2′-bipyridyl). Since the compound thus appears to contain four carbonyl groups, one nitrogen atom of the terpyridyl remains unco-ordinated. The analogous compounds $Mo(CO)_4(\text{Terpy})$ and $W(CO)_4(\text{Terpy})$, which were more stable than the chromium complex, were prepared readily by heating the ligand with the hexacarbonyls, either in the presence or absence of a solvent. The compound $Mo(CO)_3(\text{Terpy})$, on the other hand, was obtained by heating the complex $Mo(CO)_3(\text{mesitylene})$ with the ligand at 130°. Attempts to make the analogous chromium and tungsten compounds by the same method yielded only decomposed material and the tetracarbonyl complex $W(CO)_4(\text{Terpy})$, respectively.

As a further example of a compound containing a bidentate terpyridyl group, the reaction of the ligand with bromopentacarbonylmanganese was studied, since it is known that only two carbonyl groups can be replaced readily. Indeed, the tricarbonyl compound $Mn(CO)_3(\text{Terpy})Br$ has been isolated, and its i.r. spectrum in the C–O stretching region is identical with that of $Mn(CO)_3(\text{Bipy})Br$.[7]

EXPERIMENTAL

*Pentacarbonyl-*2,6-*dimethylpyrazinechromium*(0).—Hexacarbonylchromium (0·22 g.) and 2,6-dimethylpyrazine (0·11 g.) were heated in a sealed tube for 6 hr. at 100°. Unreacted starting materials were removed by sublimation and the *product* (0·20 g.) was crystallised from ethanol and dried *in vacuo* (Found: C, 44·2; H, 2·8; Cr, 16·8; N, 9·25. $C_{11}H_8CrN_2O_5$ requires C, 44·0;

---

[4] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 533.

[5] H. Behrens and U. Anders, *Z. Naturforsch.*, 1964, **19b**, 767.

[6] M. H. B. Stiddard, *J.*, 1962, 4712.

[7] E. W. Abel and G. Wilkinson, *J.*, 1959, 1501.

H, 2·7; Cr, 17·3; N, 9·3%). The compound, together with the following analogous complexes of molybdenum and tungsten, is soluble in acetone, chloroform, benzene, ethanol, and nitrobenzene; it decomposes on exposure to air and moisture.

Pentacarbonyl-2,6-*dimethylpyrazinemolybdenum*(0).—Hexacarbonylmolybdenum (0·26 g.) and 2,6-dimethylpyrazine (0·11 g.) were treated as above for 6 hr. at 120°. Similar treatment to that outlined above yielded the *product* (0·26 g.), which was dried *in vacuo* (Found: C, 38·3; H, 2·45; Mo, 27·7; N, 8·1. $C_{11}H_8MoN_2O_5$ requires C, 38·4; H, 2·3; Mo, 27·9; N, 8·1%).

Pentacarbonyl-2,6-*dimethylpyrazinetungsten*(0).—Hexacarbonyltungsten (0·35 g.) and 2,6-dimethylpyrazine (0·11 g.) were treated as above for 8 hr. at 130°. Similar treatment yielded the *product* (0·32 g.), which was dried *in vacuo* (Found: C, 30·9; H, 2·1; N, 7·3; W, 41·2. $C_{11}H_8N_2O_5W$ requires C, 30·55; H, 1·85; N, 6·5; W, 42·5%).

Tricarbonyltris-(2,6-*dimethylpyrazine*)*molybdenum*(0).—Tricarbonylmesitylenemolybdenum (0·30 g.) and 2,6-dimethylpyrazine (0·36 g.) were heated in a sealed tube at 60° for 3 hr. The product (0·42 g.) was washed with light petroleum and dried *in vacuo* (Found: C, 49·95; H, 4·8; Mo, 18·9; N, 16·7. $C_{21}H_{24}MoN_6O_3$ requires C, 50·0; H, 4·8; Mo, 18·9; N, 16·6%). The compound, together with the tungsten analogue, is sensitive to air and unstable in solution.

Tricarbonyltris-(2,6-*dimethylpyrazine*)*tungsten*(0).—Tricarbonylmesitylenetungsten (0·35 g.) and 2,6-dimethylpyrazine (0·34 g.) were treated as above at 80° for 3 hr. The *product* (0·48 g.) was washed with light petroleum and dried *in vacuo* (Found: C, 41·9; H, 4·9; N, 13·7; W, 32·0. $C_{21}H_{24}N_6O_3W$ requires C, 42·5; H, 4·5; N, 14·2; W, 31·1%).

Tetracarbonyl-2,2′,2″-*terpyridylchromium*(0).—A solution of the hexacarbonyl (0·22 g.) and the terpyridyl (0·23 g.) in isopentane (50 ml.) was exposed to u.v. light for 6 hr. After removal of the solvent, the *product* (0·17 g.) was dried *in vacuo* (Found: C, 57·5; H, 2·8. $C_{19}H_{11}CrN_3O_4$ requires C, 57·4; H, 2·8%). The compound is air-sensitive and rapidly decomposes in common organic solvents.

Tetracarbonyl-2,2′,2″-*terpyridylmolybdenum*(0).—Hexacarbonylmolybdenum (0·26 g.) and the terpyridyl (0·23 g.) were (i) heated in a sealed tube for 4 hr. at 100°, or (ii) heated in boiling xylene (50 ml.) for 2 hr., or (iii) dissolved in pentane (50 ml.) and exposed to u.v. light for 4 hr. The *product* (0·35, 0·35, and 0·23 g., respectively) was washed with light petroleum and dried *in vacuo* (Found: C, 51·1; H, 2·5; Mo, 21·1; N, 9·3. $C_{19}H_{11}MoN_3O_4$ requires C, 51·7; H, 2·9; Mo, 21·7; N, 9·5%). The properties are very similar to those of the corresponding tetracarbonyl-2,2′-bipyridyl derivative.

Tricarbonyl-2,2′,2″-*terpyridylmolybdenum*(0).—The compound $Mo(CO)_3$(mesitylene) (0·30 g.) and the terpyridyl (0·23 g.) were heated in a sealed tube at 120° for 2 hr. The *product* (0·29 g.) was washed with light petroleum and dried *in vacuo* (Found: C, 52·1; H, 2·6; Mo, 22·9; N, 10·4. $C_{18}H_{11}MoN_3O_3$ requires C, 52·0; H, 2·7; Mo, 22·3; N, 10·2%). The compound is stable to air and to moisture and is virtually insoluble in all common organic solvents.

Tetracarbonyl-2,2′,2″-*terpyridyltungsten*(0).—Hexacarbonyltungsten (0·35 g.) and the terpyridyl (0·23 g.) were either (i) heated in a sealed tube at 120° for 6 hr., or (ii) heated in boiling xylene (50 ml.) for 2 hr. The *product* (0·36 and 0·37 g., respectively) was washed with light petroleum and dried *in vacuo* (Found: C, 41·85; H, 2·7; N, 7·8; W, 34·0. $C_{19}H_{11}N_3O_4W$ requires C, 43·1; H, 2·7; N, 7·9; W, 34·7%). The properties are very similar to those of the molybdenum analogue.

Bromotricarbonyl-2,2′,2″-*terpyridylmanganese*(I).—Bromopentacarbonylmanganese (0·27 g.) and the terpyridyl (0·23 g.) were heated in boiling light petroleum (b. p. 80—100°) (50 ml.) for 2 hr. The *product* (0·34 g.), which separated, was washed with light petroleum and dried *in vacuo* (Found: C, 48·4; H, 2·6; Br, 18·2; Mn, 11·7; N, 9·1. $C_{18}H_{11}BrMnN_3O_3$ requires C, 47·8; H, 2·4; Br, 17·6; Mn, 12·1; N, 9·2%). The properties are very similar to related bromotricarbonylmanganese complexes.

We thank the Vice-Chancellor of Osmania University, Hyderabad, for granting leave of absence to M. C. G.

William Ramsay and Ralph Forster Laboratories, University College,
Gower Street, London W.C.1.

[*Received, April* 9*th*, 1965.]