Syntheses of Carbon Monoxide, Cyclopentadienyl and Related Compounds of Transition Metals Containing the η^1- or η^2-Dimethylaminomethyl Ligand †

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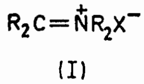
A series of chromium, molybdenum, tungsten, and iron carbonyl and substituted carbonyl compounds containing the dimethylaminomethyl, CH_2NMe_2, ligand has been synthesized using the reactive immonium compound, dimethyl(methylene)ammonium iodide. The dimethylaminomethyl group has been shown to function as a one-electron donor in compounds such as $(\eta^5\text{-}C_5H_5)Mo(CO)_3(\eta^1\text{-}CH_2NMe_2)$ and as a three-electron donor ligand in compounds such as $[Mo(CO)_3(bipy)(\eta^2\text{-}CH_2NMe_2)]^+I^-$.

Interaction of Cr and Fe carbonyl dianions with the immonium compound has been shown to form metal–carbene compounds.

In searching for new types of transition-metal alkyls we considered using immonium-type compounds (I) with their known enhanced reactivity[1] over ordinary alkyl halides to form stable metal alkyls (II). A suitable



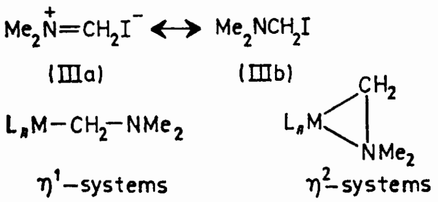
$R_2C{=}\overset{+}{N}R_2X^-$

(I)

$L_nM{-}CR_2{-}NR_2$

(II)

precursor for such syntheses seemed to be dimethyl(methylene)ammonium iodide (III),‡ a stable white solid which has the desirable properties of exhibiting moderately strong electrophilic character [by virtue of canonical form (IIIa) strongly contributing to its structure] yet being able to form metal to carbon σ bonds due to its incipient electrophilicity. Hence we may expect to synthesize compounds of type (IV). However, with the



$Me_2\overset{+}{N}{=}CH_2I^- \longleftrightarrow Me_2NCH_2I$

(IIIa) (IIIb)

$L_nM{-}CH_2{-}NMe_2$

η^1-systems

(IV)

η^2-systems

(V)

strongly donating dimethylamino-group β to the metal in σ-alkyls (IV), we could also expect to obtain a new class of three-electron donor ligand, as in (V). Systems (IV) and (V) can be considered to be analogous to the well known η^1-allyl and η^3-allyl systems, and we would expect (III) to show the same sort of enhanced reactivity over alkyl halides that allyl halides display.

We report here a series of novel organometallic compounds of types (IV) and (V) using the readily available precursor (III). Whilst our studies were in progress, the crystal structure of a similar manganese compound was described; however, this was obtained in a quite different way from compounds reported here, through the use of a dialkylaminomethyltrimethyltin precursor.[2] Mason and Rucci[3] have also claimed that the dimethylaminomethyl group acts as a π-type ligand in Cu^I complexes of dimethyl(methylene)ammonium bromide.

In the hope of synthesizing stable metal-alkyls such as (VI) or (VII), we treated some metal-carbonyl dianions with (III), but unexpectedly obtained the corresponding carbene compounds (VIII). Some of the

$L_nM(CH_2NMe_2)_2$ (VI)

$L_nM(CH_2NMe_2)^-$ (VII)

$L_nM{-}CH{-}NMe_2$ (VIII)

carbene compounds we obtained have been synthesized previously[4] by interaction of metal–carbonyl dianions with chloroform-iminium halides (IX), $Me_2\overset{+}{N}{=}CH{-}ClX^-$.

RESULTS AND DISCUSSION

As examples of σ-alkyls, we have prepared tricarbonyl-η^5-cyclopentadienyl(η^1-dimethylaminomethyl)-molybdenum and tricarbonyl-η^5-cyclopentadienyl(η^1-dimethylaminomethyl)tungsten by reacting (III) with sodium tricarbonyl-η^5-cyclopentadienylmolybdate and the corresponding tungsten analogue respectively. Both compounds are readily characterized by their solution i.r. and n.m.r. spectra (Table 2). Refluxing a light petroleum solution of tricarbonyl-η^5-cyclopentadienyl(η^1-dimethylaminomethyl)molybdenum produces dicarbonyl-η^5-cyclopentadienyl(η^2-dimethylaminomethyl)molybdenum, a compound which has also been prepared by another route, discussed below. However prolonged refluxing of a light petroleum solution (80 °C) of dicarbonyl-η^5-cyclopentadienyl(η^1-dimethylaminomethyl)tungsten does not produce the η^2-dimethylaminomethyl compound.

It has been previously shown by Hayter[5] that tris(acetonitrile)tricarbonylmetal complexes of Mo and

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† No reprints available.

‡ The interaction of $Me_2N{\cdot}CH_2Cl$ with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ and $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ has been stated to give the coupled products $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2$ and $\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2$, and a small quantity of an unstable, unidentified brown liquid in the iron case (R. B. King and H. B. Bisnette, *Inorg. Chem.*, 1966, **5**, 293).

[1] P. A. S. Smith, 'The Chemistry of Open-Chain Organic Nitrogen Compounds,', W. A. Benjamin, N.Y., 1965, vol. 1, ch. 7.

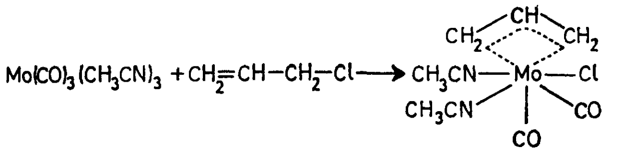
[2] E. W. Abel, R. J. Rowley, R. Mason, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1974, 72.

[3] R. Mason and G. Rucci, *Chem. Comm.*, 1971, 1132.

[4] B. Cetinkaya, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1972, 851.

[5] R. G. Hayter, *J. Organometallic Chem.*, 1968, **13**, 1.

W are useful precursors for forming η^3-allylmetal-carbonyls. For example:



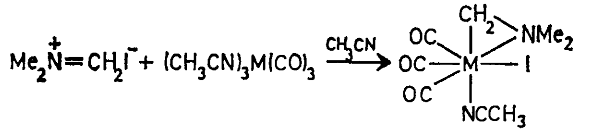
TABLE

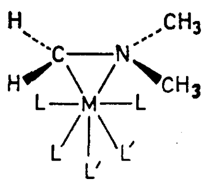
Analytical and spectroscopic data

Compound [a]	Analyses (%)								N.m.r. data [b] (in p.p.m.)	CO Stretching frequency (in cm^{-1})
	Calc.				Found					
	C	H	N	I	C	H	N	I		
(cp)$Mo(CO)_3(\eta^1$-L) [c]	43·6	4·3	4·6		44·5	4·1	4·5		5·64(5), 2·32(2), 2·36(6) [d]	2037m, 1969s, 1953m, sh [e]
(cp)$W(CO)_3(\eta^1$-L)	33·8	3·3	3·6		33·5	3·3	3·7		5·72(5), 2·32(2), 2·38(6) [d]	2045s, 1961vs, 1945s, sh [e]
(η^2-L)$Mo(CO)_3(CH_3CN)$I	23·6	2·7	6·9	31·3	24·0	3·0	6·8	31·0	3·08, 3·00, 2·95 [g]	2000s, 1930vs, 1840vs [f]
(η^2-L)$W(CO)_3(CH_3CN)$I	19·4	2·2	5·7	25·7	20·1	2·5	5·8	26·2	3·15, 3·10 [g]	2000s, 1920vs, 1835vs [f]
[(η^2-L)$Mo(CO)_3$(bipy)]$^+I^-$	36·9	3·1	8·1	24·4	37·1	2·8	7·9	24·0	2·16(6), 2·00(2) [d]	2010w, 1875vs, 1815vs [f]
[(η^2-L)$Mo(CO)_3$(diphos)]$^+[OC(O)CF_3]^-$	47·0	3·5	1·5		46·8	3·7	1·7		2·05(6), 1·47(2) [g]	2015w, 1920vs, 1829vs, 1785vs, 1675s [f]
[(η^2-L)$W(CO)_3$(bipy)]$^+I^-$	31·5	2·6	6·9	20·85	31·1	2·7	7·2	20·5	2·08(6), 1·96(2) [d]	2010w, 1870vs, 1810vs [f]
[(η^2-L)$W(CO)_3$(phen)]$^+I^-$	34·1	2·5	6·6	20·1	33·9	2·6	6·7	21·1	1·98(2), 1·98(6) [d]	2017w, 1889vs, 1769vs [f]
(cp)$Mo(CO)_2(\eta^2$-L)	43·6	4·7	5·1		43·3	4·6	4·7		5·36(5), 2·69(6), 2·52(2) [d]	1936s, 1844s [e]
$Fe(CO)_4(CHNMe_2)$	37·3	3·1	6·2		37·4	3·1	6·2		3·54(3), 3·68(3), 11·14(1) [d]	2049s, 1977s, 1949vs, 1937vs [e]
$Cr(CO)_5(CHNMe_2)$	38·6	2·8	5·6		38·7	2·9	5·6		3·55(3), 3·73(3), 10·90(1) [d]	2057m, 1970w, 1941sh, s, 1933vs [e]
$Cr(CO)_5\{CHN(C_5H_{10})\}$	45·7	3·8	4·8		45·8	3·7	4·6		0·93(2), 1·30(4), 1·87(4), 3·77(2), 4·20(2), 10·76(1) [d]	2055m, 1969w, 1935sh, sh, 1931vs
[(η^2-L)$Fe(CO)_4]^+[BPh_4]^-$	68·1	5·1	2·6		69·0	5·4	2·3		2·20(2), 2·30(6) [d]	2085w, 2037sh, vs, 2026vs,[h] 2011sh

[a] L = $-CH_2N(CH_3)_2$. [b] Relative to tetramethylsilane, at 35 °C; values in parentheses refer to integrated values. [c] cp = η^5-C_5H_5. [d] $CDCl_3$ solution. [e] Cyclohexane solution. [f] Nujol mull. [g] CH_2Cl_2 solution. [h] [$^2H_6$]Acetone solutions.

Hence as system (V) is potentially isoelectronic with the η^3-allyl system, we expected the reaction of $M(CO)_3(CH_3CN)_3$ to proceed similarly. The products actually obtained in good yields by interaction of (III) with $M(CO)_3(CH_3CN)_3$ (M = Mo or W) were acetonitrile-tricarbonyl(η^2-dimethylaminomethyl)iodomolybdenum (IX) and the tungsten analogue (X). These formulations were confirmed by analytical data and the presence of three bands in the i.r. spectra at 2000s, 1930vs, and 1840vs cm^{-1} for (IX), and at 2000s, 1930vs, and 1835vs cm^{-1} (±5 cm^{-1}) for (X). The close similarity of the i.r. spectra in the metal–carbonyl range is matched in the region 1800—400 cm^{-1}, the spectra being identical with respect to band intensities and number of bands, but showing shifts in the position of some bands by no more than ±5 cm^{-1}. The n.m.r. spectrum of (IX) in [$^2H_6$]acetone shows peaks at 3·00, 3·08, and 2·95 p.p.m. in order of descending intensity. However, these peaks are not clearly resolved at 100 MHz. The situation is complicated by the possibility of non-equivalence of the methylene protons, and the $N-CH_3$ protons as in (XI), owing to dissymmetry at the metal induced by the various ligands. The problem is further complicated by the possibility of differing proportions of isomers. However the intensities roughly suggest the peaks at 2·95, 3·00, and 3·08 p.p.m. correspond respectively to the methylene, the two *N*-methyl protons, and the methyl protons of acetonitrile of one major isomer.



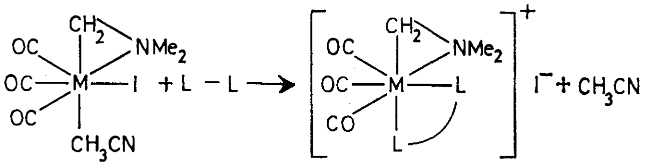


(XI)

This suggests if these assignments are valid, that magnetic dissymmetry at the metal is insufficient to manifest itself. Other examples of the non-observation of potential magnetic inequivalence of the η^2-dimethylaminomethyl ligand will be given later. The n.m.r. spectra of (X) is similar to its molybdenum analogue (IX). The postulation of 7-co-ordinate Mo and W compounds is not unusual, as Hayter[5] and Hull and Stiddard[6] have authenticated many examples of compounds of the type (η^3-CH_2=CH-CH_2)M(CO)$_2$L$_2$X (M = Mo or W) which are 7-co-ordinate.

Attempts to prepare [(η^2-Me_2NCH_2)Mo(CO)$_3$-(CH_3CN)$_2$]$^+$$BF_4^-$ and the tungsten analogue by using (CH_3CN)$_3$M(CO)$_3$ and ($Me_2\overset{+}{N}$=CH_2)BF_4^- were unsuccessful, only starting materials being isolated, implicating a pre-requisite nucleophilic attack by iodide ion as the initial step.

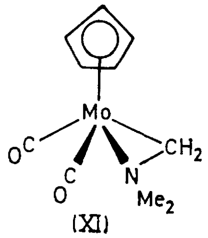
Both compounds (IX) and (X) react rapidly with bidentate ligands (L-L) such as 2,2′-bipyridyl, 1,10-phenanthroline, and 1,2-bis(diphenylphosphine)ethane to give salts:



The retention of three carbonyls can be seen clearly in the i.r. spectra of these compounds, while the resonances of the methylene and the *N*-methyl protons shift upfield from the region of 2·9—3·2 p.p.m. for compounds (IX) and (X) to the region of 2·0—2·2 p.p.m. upon chelation by the bidentate ligands, indicating a substantial reduction in electron density at the metal. The iodide ion can be exchanged for the trifluoroacetate anion, the i.r. and n.m.r. spectra remaining essentially unchanged. Conductivity measurements in nitromethane gave values a little lower than those expected for a 1 : 1 electrolyte, owing to some decomposition of the solutions.

The pale yellow salt [(η^2-Me_2NCH_2)Mo(CO)$_3$(diphos)] [CF_3CO_2]·2CH_2Cl_2 appears to be a mixture of at least two isomers, judging from the i.r. spectrum, which shows bands at 2015w, 1920vs, 1829vs, and 1785vs cm^{-1} which can be assigned to ν(M-CO). A broad strong band at 1675 cm^{-1} can be assigned to the carboxylate stretch of the trifluoroacetate group, being only slightly different from the values for silver trifluoroacetate (1665 cm^{-1}) and sodium trifluoroacetate (1685 cm^{-1}) (Nujol). The n.m.r. spectrum in [$^2H_6$]acetone shows a broad signal at 1·47 p.p.m., and a singlet at 2·05 p.p.m. (superimposed on the solvent peak). These can be assigned to the methylene and *N*-methyl protons respectively. Upon closer examination, the 1·47 p.p.m. signal is a complex multiplet, the splitting being barely resolvable at 100 MHz. Such splitting can be attributed to long range ^{31}P-M-C-^{1}H coupling by the two phosphorus atoms. A sharp singlet at 5·62 p.p.m. has an intensity corresponding well on integration for two CH_2Cl_2 of crystallization in confirmation of the analytical data.

Compound (IX) also reacts with sodium cyclopentadienide in tetrahydrofuran to give a moderate yield of (η^5-C_5H_5)Mo(CO)$_2$(η^2-CH_2NMe_2) (XI); this readily sublimes and the 70 eV mass spectrum confirms its identity.



(XI)

The compound shows only three sharp singlets at 5·36, 2·69, and 2·52 p.p.m., assignable to the η^5-C_5H_5, NMe_2, and CH_2 groups respectively. Again the consequences of possible magnetic inequivalence of the η^2-CH_2NMe_2 group are not apparent.

Prolonged refluxing of an acetonitrile solution of compound (III) and pentacarbonyliron produces a deep red solution, from which can be isolated tetracarbonyl-(η^2-*NN*-dimethylaminomethyl)iron tetraphenylborate by addition of sodium tetraphenylborate. The n.m.r. spectrum in $CDCl_3$ shows two singlets at 2·20 and 2·30 p.p.m. which can be assigned to the methylene and *N*-methyl protons respectively. These values are similar to those of the cationic molybdenum and tungsten compounds, (IX) and (X). Prolonged refluxing of a tetrahydrofuran solution of (III) and pentacarbonyliron gave no reaction, implicating an intermediate acetonitrile-iron complex. In a rather similar reaction,[8] allyl iodide reacts with pentacarbonyliron to give η^3-allyltricarbonyliodoiron.

Lappert *et al.*[4] have previously shown that reaction between metal-carbonyl dianions and chloroformiminium chlorides produce secondary carbenes. We have found that reaction of (III) with disodium tetracarbonylferrate and disodium pentacarbonylchromate produce moderate yields of the carbene complexes, Fe(CO)$_4$(CHNMe$_2$) and Cr(CO)$_5$(CHNMe$_2$), presumably by hydrogen abstraction from one $FeCH_2NMe_2$ group by a second to give NMe_3. The properties of these compounds are in good agreement with those previously reported.[4] Reaction between the pentacarbonylchromium dianion and piperidyl(methylene)ammonium chloride gives a low yield of the carbene compound, Cr(CO)$_5${CHN(cyclo-C_5H_{10}}. The highly deshielded hydrogen atom attached to C (carbene) resonates at 10·76 p.p.m. The two non-equivalent methylene groups α to the N of the piperidine moiety appear at 3·77 and 4·20 p.p.m. as broad signals. Magnetic non-equivalence of two sets of alkyl groups attached to N, have been previously observed,[4] and is due to a high C-N bond order. Reaction between the tetracarbonyliron dianion and ($Me_2\overset{+}{N}$CHSMe)Br^- in tetrahydrofuran again produces the carbene compound Fe(CO)$_4$(CHNMe$_2$) in low yields and {$Me_2SFe(CO)_3$}$_2$.

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[6] C. G. Hull and M. H. B. Stiddard, *J. Organometallic Chem.*, 1967, **9**, 519.

[7] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[8] R. A. Plowman and F. G. A. Stone, *Z. Naturforsch.*, **1962**, **17b**, 575.

EXPERIMENTAL

General Procedures.—All manipulations were carried out under pure nitrogen or argon, using freshly distilled, dry, degassed solvents.

^{1}H N.m.r. spectra were recorded on Perkin-Elmer R-14 (100 MHz) and Perkin-Elmer R-12A (60 MHz) spectrometers. I.r. spectra were measured on Perkin-Elmer 257 or 457 spectrometers, solids as Nujol mulls or as KBr discs, and solution spectra in 0·1 mm compensated liquid cells. The spectra were calibrated using a polystyrene film. Mass spectra were obtained using an A.E.I. MS9 spectrometer.

Dimethyl(methylene)ammonium iodide was prepared by the method of Eschenmoser.[9] Dimethyl(methylene)ammonium chloride and dimethyl(methylene)ammonium fluoroborate were obtained using the procedure of Bohm and Hartke,[10] by allowing *NNN'N'*-tetramethyldiaminomethane to react with acetyl chloride and acetyl fluoride/boron trifluoride–diethyl ether respectively. *N*-Chloromethylpiperidine was obtained by the method of Bohm and Hartke [10] by treating dipiperidinomethane with acetyl chloride in ether. Dipiperidinomethane was prepared by condensing formaldehyde with piperidine in the ratio 1 : 2 molar, according to the standard procedure.[11]

Tris(acetonitrile)tricarbonylmolybdenum and tris(acetonitrile)tricarbonyltungsten were obtained by the standard procedures.[12] The compounds were not isolated but were used as acetonitrile solutions, after the solution i.r. spectra were shown to be identical with the literature data in the region 2100—1600 cm^{-1}.

Syntheses

Acetonitriletricarbonyl(η^2-NN-*dimethylaminomethyl*)*iodomolybdenum.*—To an acetonitrile solution of tris(acetonitrile)tricarbonylmolybdenum (0·01 mol in *ca.* 150 ml) was added solid dimethylmethyleneammonium iodide (0·01 mol) and the suspension was stirred at room temperature for three days. The suspension gradually became a homogeneous orange solution after *ca.* 1 day. The solution was filtered and concentrated *in vacuo* to *ca.* 20 ml. Upon the addition of ether (*ca.* 50 ml), brownish red crystals began to separate from solution. The solid was filtered off and dried *in vacuo*; yield, 2·6 g (65%). Although the brownish red compound is stable for long periods as a solid under an inert atmosphere, acetone, dichloromethane, and tetrahydrofuran solutions of it decompose rapidly in the presence of air.

Acetonitriletricarbonyl(η^2-NN-*dimethylaminomethyl*)*iodotungsten.*—Solid dimethylmethyleneammonium iodide (0·01 mol) was added to an acetonitrile solution of tris(acetonitrile)tricarbonyltungsten (0·01 mol in *ca.* 150 ml) and the suspension was stirred for *ca.* 3 days. The suspension gradually became a red homogeneous solution after *ca.* 1 day. The solution was filtered and concentrated *in vacuo* to *ca.* 20 ml, whereupon red-brown plate-like crystals separated out. The crystals were filtered off and dried *in vacuo*. Addition of ether to the filtrate produced further red-brown crystals with time; yield, 3·0 g, 61%. Although the solid compound is stable for long periods under an inert atmosphere, acetone, dichloromethane, and tetrahydrofuran solutions of it decompose rapidly in air, but not as quickly as its molybdenum analogue.

2,2'-Bipyridyltricarbonyl(η^2-NN-*dimethylaminomethyl*)-*iodomolybdenum.*—To an acetonitrile or dichloromethane solution of acetonitriletricarbonyl(*NN*-dimethylaminomethyl)iodomolybdenum was added an acetonitrile or dichloromethane solution of 2,2'-bipyridyl. A reddish brown precipitate immediately formed. The crystals were filtered off, washed, and then dried *in vacuo*; yields were in the range 80—90%. Although the solid compound is reasonably stable to air, solutions in acetone and methylene chloride rapidly turn purplish blue on exposure to air.

1,2-Bis(diphenylphosphino)ethanetricarbonyl(η^2-NN-*dimethylaminomethyl*)*molybdenum Trifluoroacetate–Bis(dichloromethane).*—Solid 1,2-bis(diphenylphosphine)ethane (1·99 g, 0·005 mol) was added to an acetonitrile solution of acetonitriletricarbonyl(*NN*-dimethylaminomethyl)iodomolybdenum (0·005 mol). The reddish solution gradually became yellow. Solid silver trifluoroacetate (1·1 g, 0·005 mol) was added, and the suspension was stirred for 2 days. The solvent was removed under vacuum, and dichloromethane was added. Slow removal of the solvent precipitate pale yellow crystals of the compound; yield 3·3 g, 80%. The solid compound is quite air stable, and both the solid and acetone and methylene chloride solutions are far more resistant to oxidation than 2,2'-bipyridyltricarbonyl-(dimethylaminomethyl)iodomolybdenum.

2,2'-Bipyridyltricarbonyl(η^2-NN-*dimethylaminomethyl*)-*iodotungsten.*—This complex was prepared similarly to its molybdenum analogue in 83% yield. The compound forms reddish brown crystals which are reasonably air stable. However, acetone or methylene chloride solutions rapidly turn violet-blue on exposure to air.

Tricarbonyl(η^2-NN-*dimethylaminomethyl*)-1,10-*phenanthrolinetungsten.*—This complex forms reddish brown crystals which are reasonably air stable, but acetone or methylene chloride solutions rapidly turn violet-blue on exposure to air.

Tricarbonyl-η^5-*cyclopentadienyl*(η^1-NN-*dimethylaminomethyl*)*molybdenum.*—To a solution of sodium tricarbonyl-η^5-cyclopentadienylmolybdate (0·01 mol) in tetrahydrofuran (100 ml) was added solid dimethyl(methylene)ammonium iodide (1·84 g, 0·01 mol), and the suspension was stirred overnight to form a homogeneous solution. After removal of solvent under vacuum and addition of light petroleum, the yellow solution was filtered. The light petroleum solution was reduced in volume, and upon cooling to −70 °C yellow crystals were deposited (1·6 g, 53%).

Tricarbonyl-η^5-*cyclopentadienyl*(η^1-NN-*dimethylaminomethyl*)*tungsten.*—This complex was prepared similarly to its molybdenum analogue, using sodium tricarbonyl-η^5-cyclopentadienyltungstate, in 60% yield as yellow crystals.

Dicarbonyl-η^5-*cyclopentadienyl*(η^2-NN-*dimethylaminomethyl*)*molybdenum.*—To a tetrahydrofuran solution of acetonitriletricarbonyl(η^2-*NN*-dimethylaminomethyl)iodomolybdenum (2·03 g, 0·005 mol) was added sodium cyclopentadienide (0·44 g, 0·005 mol) in tetrahydrofuran. The solution immediately went yellow. Removal of the solvent followed by careful sublimation at 40—50 °C at 0·05 mmHg yielded the compound (0·6 g, 43% yield) as yellow crystals. The mass spectrum at 70 eV (50 °C) shows a strong molecular ion at *m/e* 277, 34% relative abundance. Other peaks and assignments are *m/e* 260 (19%) cpMo(CO$_2$)C$_3$H$_5$, *m/e* 249 (42%) cpMo(CO)CH$_2$NMe$_2$, *m/e* 232 (23%) cpMo(CO)C$_3$H$_5$,

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[9] J. Schreiber, H. Maag, N. Hashimoto, and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1971, **10**, 330.

[10] H. Bohm and K. Hartke, *Chem. Ber.*, 1960, **93**, 1305.

[11] N. J. Putochin, *Ber.*, 1922, **55B**, 2749.

[12] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

m/e 219 (100%) cpMo(CO)$_2$, m/e 204 (28%) cpMoC$_3$H$_5$, m/e 202 (46%) cpMoC$_3$H$_3$, m/e 191 (42%) cpMoCO, m/e 163 (47%) cpMo, m/e 137 (21%) MoC$_3$H$_3$, m/e 98 (22%) Mo, and m/e 58 (61%) CH$_2$NMe$_2$.

Tetracarbonyl(dimethylaminomethyl)iron Tetraphenylborate.—A suspension of dimethyl(methylene)ammonium iodide (1·84 g, 0·01 mol) and pentacarbonyliron (1·34 ml, 0·01 mol) in acetonitrile (40 ml) was heated to reflux, whereupon the mixture became homogeneous. Upon prolonged refluxing, the solution gradually became red. After 3 days of refluxing, the reaction was complete as indicated by i.r. monitoring of the solution. Solid sodium tetraphenylborate (3·42 g, 0·01 mol) was added and refluxing was continued for a further 3 days. The acetonitrile was removed under vacuum, and dichloromethane (60 ml) was added. The solution was filtered to remove inorganic salts and metallic iron. As the solvent was slowly removed, brownish red crystals of the product were deposited (1·1 g, 10% yield). The solid compound appears to be reasonably stable to air, and acetone or dichloromethane solutions decompose fairly slowly upon exposure to air.

Tetracarbonyldimethylaminomethyleneiron.—To a tetrahydrofuran solution of disodium tetracarbonylferrate (0·01 mol) was added solid dimethyl(methylene)ammonium iodide (1·84 g, 0·01 mol) and the suspension was stirred for 16 h. Upon removal of the solvent under vacuum, the compound was sublimed at 40—50 °C at 0·01 mmHg to afford yellow crystals (0·7 g, 30%). The mass spectrum at 70 eV (80 °C) shows a strong molecular ion at m/e 225 (21%). The base peak is m/e 197 (29%); peaks at 169 (5%) and 141 (35%) can be assigned to successive loss of CO.

Pentacarbonyldimethylaminomethylenechromium.— This complex was prepared similarly to the iron carbene compound, but using the pentacarbonylchromium dianion in 20% yield. The yellow compound sublimes easily at 0·01 mmHg (40—50 °C). The mass spectrum at 70 eV (50 °C) shows a strong molecular ion at m/e 249 (17%). The base peak is m/e 109 (100%), assigned to CrCHNMe$_2$. Peaks at m/e 221 (5%), 193 (3%), 165 (5%), and 137 (20%) are due to successive loss of CO.

Pentacarbonylpiperidylmethylenechromium.—This complex was prepared similarly to pentacarbonyldimethylaminomethylenechromium, in 10% yield. The yellow compound sublimes at 70—80 °C at 0·01 mmHg. The mass spectrum at 20 eV (70 °C) shows a molecular ion at m/e 289 (100%). Other ions at m/e 261 (32%), 233 (40%), 205 (28%), 177 (42%), and 149 (4%) represent successive loss of five CO.

Reaction between Methyl N-*Methylthioformimidate Methobromide and Disodium Tetracarbonylferrate.*—To a tetrahydrofuran solution of disodium tetracarbonylferrate (0·01 mol) was added solid methyl *N*-methylthioformimidate methobromide (1·84 g, 0·01 mol) and the suspension stirred overnight. The solution eventually turned deep red. After removal of the solvent under vacuum, a deep red oil sublimes easily at 30—40 °C at 0·01 mmHg. Upon further heating 50—60 °C, a mixture of the red oil and tetracarbonyldimethylaminomethyleneiron sublimes. The carbene compound can be recrystallized pure from light petroleum. The red oil, crystallized from light petroleum and resublimed, shows identical spectroscopic properties with a genuine sample of {MeSFe(CO)$_3$}$_2$.

Dicarbonyl-η^5-cyclopentadienyl(η^2-dimethylaminomethyl)-molybdenum.—A light petroleum (60—80 °C) solution of η^5-cyclopentadienyl(η^1-dimethylaminomethyltricarbonyl)-molybdenum was refluxed overnight. The solvent was removed under vacuum and the compound sublimed from the residue at 40—50 °C at 0·05 mmHg. The compound showed identical i.r., n.m.r., and mass spectral properties as the compound prepared by allowing sodium cyclopentadienide to react with tricarbonyl(η^2-*NN*-dimethylaminomethyl)iodomolybdenum. U.v. photolysis of a light petroleum solution of tricarbonyl-η^5-cyclopentadienyl(η^1-dimethylaminomethyl)molybdenum produced only {η^5-C$_5$H$_5$)Mo(CO)$_3$}$_2$.

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