

Preparation of halogenated arene complexes and their dehalogenation for further metallation

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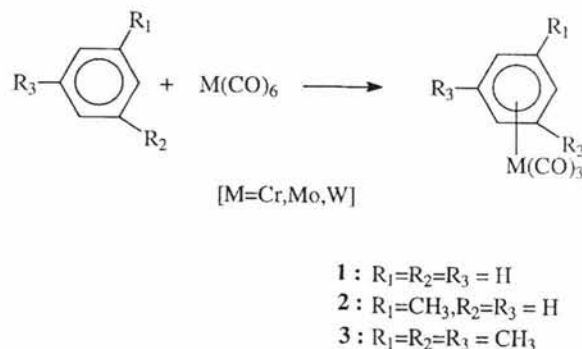
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Reaction of *tris*(acetonitrile)molybdenumtricarbonyl $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ and *tris*(acetonitrile)chromiumtricarbonyl $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ with 1,2,4,5-*tetrakis* (bromomethyl) benzene and 1,2,3,4,5,6-*hexakis*(bromomethyl)benzene yield complexes $[\text{C}_6\text{H}_2(\text{CH}_2\text{Br})_4\text{Mo}(\text{CO})_3]$ (4), $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Mo}(\text{CO})_3]$ (5), $[\text{C}_6\text{H}_2(\text{CH}_2\text{Br})_4\text{Cr}(\text{CO})_3]$ (6) and $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Cr}(\text{CO})_3]$ (7) respectively. The halogenated arene complexes (4), (6) and (5) on treatment with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ at room temperature form of the complexes $[\text{C}_6\text{H}_2(\text{CH}_2)_4\{\text{Fe}(\text{CO})_4\}_2\text{Mo}(\text{CO})_3]$ (8), $[\text{C}_6\text{H}_2(\text{CH}_2)_4\{\text{Fe}(\text{CO})_4\}_2\text{Cr}(\text{CO})_3]$ (9) and $[\text{C}_6(\text{CH}_2)_6\{\text{Fe}(\text{CO})_4\}_3\text{Mo}(\text{CO})_3]$ (10) respectively. The complexes have been characterized by IR, ^1H NMR and mass spectral data.

Thermolysis of hexacarbonyls of chromium, molybdenum and tungsten in presence of arene leads to the formation of $[(\text{arene})\text{M}(\text{CO})_3]$ derivatives¹ according to reaction Scheme-I. The thermal method has, however, the disadvantage that high temperatures and long reaction times are required^{2,3}. The complexes $[(\text{arene})\text{M}(\text{CO})_3]$ ($\text{M}=\text{Cr}, \text{Mo}$ or W) can be synthesized from $[\text{L}_3\text{M}(\text{CO})_3]$ by arene/ L_3 exchange under milder conditions. Many different ligands (L) have been employed for this reaction, *e.g.* $[\text{L}=\text{CH}_3\text{CN}, \text{THF}, \text{diglyme}, \text{NH}_3 \text{ etc.}]$ ⁴.

Materials and Methods

All the reactions and subsequent handling were carried out in dry nitrogen atmosphere. Acetonitrile was distilled under nitrogen over phosphorus pentaoxide. THF was distilled under nitrogen over sodium bezophenone ketyl prior to use. $\text{Na}_2[\text{Fe}(\text{CO})_4]$ ⁵, *tris*(acetonitrile)molybdenumtricarbonyl $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ ⁶ and *tris*(acetonitrile)chromiumtricarbonyl $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ ⁷ were synthesized by the known procedure. 1, 2, 4, 5-*Tetrakis*(bromomethyl)benzene and 1, 2, 3, 4, 5, 6-*hexakis*(bromomethyl)benzene were prepared according to the known method⁸. The IR spectra were recorded on a Shimadzu 8010 spectrometer, ^1H NMR spectra on a



Scheme - I

Bruker 250 MHz spectrometer and electron impact mass spectra on a high resolution mass spectrometer.

Reaction of *tris* (acetonitrile) molybdenumtricarbonyl $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ with 1,2,4,5-*tetrakis*(bromomethyl) benzene

To a freshly prepared solution of $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ (1.46 g, 4.82 mmol) in acetonitrile (50 mL) was added a solution of 1,2,4,5-*tetrakis* (bromomethyl) benzene (2.17 g, 4.82 mmol) in the same solvent (30 mL) by a dropping funnel under nitrogen atmosphere with vigorous stirring. After completion of addition the

reactants were allowed to stir for 24 hr at room temperature. The course of the reaction was monitored by analytical TLC. The solvent was removed *in vacuo* and the residue was extracted with diethylether and filtered on kieselguhr. The mixture was then chromatographed over a column of silica gel (230-400 mesh) and the yellow band was eluted with petroleum ether (40-60°C)-diethyl ether (1:1 v/v). Removal of solvent under reduced pressure afforded $[C_6H_2(CH_2Br)_4-Mo(CO)_3]$ (**4**) as a grey solid (0.22 g, 7%); IR (cyclohexane): ν_{CO} 1950 and 1987 cm^{-1} ; ^1H NMR ($CDCl_3$): δ 4.58 (s, 8H) and δ 7.35 (s, 2H); MS: m/z 630 (no M^+), 450 [$M^+ - (3CO + Mo)$], 370 [$M^+ - (3CO + Mo + Br)$], 290 [$M^+ - (3CO + Mo + 2Br)$], 210 [$M^+ - (3CO + Mo + 3Br)$], 130 [$M^+ - (3CO + Mo + 4Br)$], 116 [$M^+ - (3CO + Mo + 4Br + CH_2)$], 115 [$M^+ - (3CO + Mo + 4Br + CH_2 + H)$].

Reaction of tris(acetonitrile)molybdenumtricarboxyl $[Mo(CO)_3(CH_3CN)_3]$ with 1,2,3,4,5,6-hexakis(bromomethyl)benzene

To a freshly prepared solution of $[Mo(CO)_3(CH_3CN)_3]$ (0.715 g, 2.36 mmol) in acetonitrile (30 mL) was added dropwise a solution of 1,2,3,4,5,6-hexakis(bromomethyl)benzene (1.5 g, 2.36 mmol) in the same solvent (30 mL) by a dropping funnel under nitrogen atmosphere with vigorous stirring. The rest of the procedure adopted was the same as described above which yielded $[C_6(CH_2Br)_6Mo(CO)_3]$ (**5**) as grey solid (0.2 g, 10%); IR (cyclohexane): ν_{CO} 1952 and 1987 cm^{-1} .

Reaction of tris(acetonitrile)chromiumtricarboxyl $[Cr(CO)_3(CH_3CN)_3]$ with 1,2,4,5-tetrakis(bromomethyl)benzene

To a freshly prepared solution of $[Cr(CO)_3(CH_3CN)_3]$ (0.864 g, 3.33 mmol) in acetonitrile was added dropwise a solution of 1,2,4,5-tetrakis(bromomethyl)benzene (1.5 g, 3.33 mmol) in the same solvent in (30 mL) by a dropping funnel under nitrogen atmosphere with vigorous stirring. The rest of the procedure adopted was same as described above which yielded $[C_6H_2(CH_2Br)_4Cr(CO)_3]$ (**6**) as a greenish-yellow solid (0.25 g, 12%); IR (cyclohexane): ν_{CO} 1925 and 1950 cm^{-1} ; MS: m/z 586 [M^+], 558 [$M^+ - CO$], 530 [$M^+ - 2CO$], 502 [$M^+ - 3CO$], 450 [$M^+ - (3CO + Cr)$], 370 [$M^+ - (3CO + Cr + Br)$], 290 [$M^+ - (3CO + Cr +$

$2Br)$], 210 [$M^+ - (3CO + Cr + 3Br)$], 130 [$M^+ - (3CO + Cr + 4Br)$], 116 [$M^+ - (3CO + Cr + 4Br + CH_2)$].

Reaction of tris(acetonitrile)chromiumtricarboxyl $[Cr(CO)_3(CH_3CN)_3]$ with 1,2,3,4,5,6-hexakis(bromomethyl)benzene

To a freshly prepared solution of $[Cr(CO)_3(CH_3CN)_3]$ (0.61 g, 2.36 mmol) in acetonitrile was added dropwise a solution of 1,2,3,4,5,6-hexakis(bromomethyl)benzene (1.5 g, 2.36 mmol) in the same solvent (30 mL) by a dropping funnel under nitrogen atmosphere with vigorous stirring. The rest of the procedure adopted was same as described above, which yielded $[C_6(CH_2Br)_6Cr(CO)_3]$ (**7**) as a greenish solid (0.305 g, 16.74%); IR (cyclohexane): ν_{CO} 1925 and 1950 cm^{-1} ; ^1H NMR ($CDCl_3$): δ 2.15 (s, 12H); MS: m/z 772 [no M^+], 236 [$M^+ - (6Br + 2CO)$], 207 [$M^+ - (6Br + 3CO + H)$], 155 [$M^+ - (6Br + 3CO + H + Cr)$].

*Reaction of $Na_2[Fe(CO)_4]$ with $[C_6H_2(CH_2Br)_4Mo(CO)_3]$ (**4**)*

To a freshly prepared suspension of $Na_2[Fe(CO)_4]$ (0.10 g, 0.46 mmol) in THF (30 mL) was added dropwise a solution of $[C_6H_2(CH_2Br)_4Mo(CO)_3]$ (**4**) (0.15 g, 0.23 mmol) in THF (20 mL) from a dropping funnel under nitrogen with vigorous stirring. After completion of addition the reactants were allowed to stir for 36 hr at room temperature. The course of reaction was monitored by analytical TLC. The solvent was removed under reduced pressure and the residue was extracted twice with 60 mL of petroleum ether (40-60°C) and filtered on kieselguhr. The mixture was then chromatographed on silica gel (230-400 mesh) eluting with petroleum ether (40-60°C) which gave only one yellowish band. The yellowish band on removal of solvent under reduced pressure afforded $[C_6H_2(CH_2)_4\{Fe(CO)_4\}_2Mo(CO)_3]$ (**8**) (0.014 g, 9.10%) as a grey solid; IR (cyclohexane): ν_{CO} 1945, 1981 cm^{-1} ; 1997 and 2049 cm^{-1} ; ^1H NMR ($CDCl_3$): δ 2.27 (s, 8H) and 6.96 (s, 2H); MS: m/z 646 [M^+], 645 [$M^+ - H$], 617 [$M^+ - (CO + H)$], 589 [$M^+ - (2CO + H)$], 561 [$M^+ - (3CO + H)$], 533 [$M^+ - (4CO + H)$], 505 [$M^+ - (5CO + H)$], 477 [$M^+ - (6CO + H)$], 449 [$M^+ - (7CO + H)$], 421 [$M^+ - (8CO + H)$], 365 [$M^+ - (8CO + Fe + H)$], 309 [$M^+ - (8CO + 2Fe + H)$], 281 [$M^+ - (8CO + 2Fe + CO + H)$], 253 [$M^+ - (8CO + 2Fe + 2CO + H)$], 225 [$M^+ - (8CO + 2Fe + 3CO + H)$], 129 [$M^+ - (8CO + 2Fe + 3CO + H + Mo)$].

Reaction of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with $[\text{C}_6\text{H}_2(\text{CH}_2\text{Br})_4\text{Cr}(\text{CO})_3]$ (6)

To a freshly prepared suspension of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (0.14 g, 0.686 mmol) in dry THF (30 mL) was added dropwise a solution of $[\text{C}_6\text{H}_2(\text{CH}_2\text{Br})_4\text{Cr}(\text{CO})_3]$ (6) (0.2 g, 0.34 mmol) in THF (20 mL) by a dropping funnel under nitrogen atmosphere with vigorous stirring. After completion of addition the reactants were stirred for 36 hr at room temperature. The course of reaction was monitored by analytical TLC. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether and filtered on kieselguhr. The mixture was then chromatographed over a column of silica gel (230-400 mesh) with petroleum ether (40-60°C)-diethylether (4:1 v/v) to obtain one yellowish band. The yellowish band on removal of solvent under reduced pressure afforded $[\text{C}_6\text{H}_2(\text{CH}_2)_4\{\text{Fe}(\text{CO})_4\}_2\text{Cr}(\text{CO})_3]$ (9) (0.021 g, 9%) as yellowish solid; IR (cyclohexane): ν_{CO} 1925, 1948 cm^{-1} ; 1985 and 2047 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.23 (s, 8H) and 7.26 (s, 2H); MS: m/z 602 [no M^+], 417 [$\text{M}^+ - (3\text{CO} + \text{H})$], 265 [$\text{M}^+ - (8\text{CO} + 2\text{Fe} + \text{H})$], 237 [$\text{M}^+ - (9\text{CO} + 2\text{Fe} + \text{H})$], 209 [$\text{M}^+ - (10\text{CO} + 2\text{Fe} + \text{H})$], 181 [$\text{M}^+ - (11\text{CO} + 2\text{Fe} + \text{H})$], 129 [$\text{M}^+ - (11\text{CO} + 2\text{Fe} + \text{Cr} + \text{H})$], 115 [$\text{M}^+ - (11\text{CO} + 2\text{Fe} + \text{Cr} + \text{H} + \text{CH}_2)$].

Reaction of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Mo}(\text{CO})_3]$ (5)

To a freshly prepared suspension of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (0.153 g, 0.715 mmol) in THF (30 mL) was added dropwise a solution of $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Mo}(\text{CO})_3]$ (5) (0.15 g, 0.23 mmol) in THF (20 mL) from a dropping funnel under nitrogen with vigorous stirring. After completion of addition the reactants were stirred for 36 hr at room temperature. The course of reaction was monitored by analytical TLC. The solvent was removed under reduced pressure and the residue was extracted twice with 50 mL portion of petroleum ether (40-60°C)/diethyl ether (1:1, v/v) and filtered on kieselguhr. The mixture was then chromatographed over a column of silica gel (230-400 mesh) and eluted with petroleum ether (40-60°C) which gave one distinct yellowish band. The band on removal of solvent under reduced pressure afforded $[\text{C}_6(\text{CH}_2)_6\{\text{Fe}(\text{CO})_4\}_3\text{Mo}(\text{CO})_3]$ (10) (10.76%) as yellowish crystals; IR (cyclohexane): ν_{CO} 1931, 1948 cm^{-1} ; 1989 and 2035 cm^{-1} . ^1H NMR (CDCl_3): δ 1.26 (s, 12H); MS: m/z 840 [M^+], 812 [$\text{M}^+ - \text{CO}$], 784 [$\text{M}^+ - 2\text{CO}$], 756 [$\text{M}^+ - 3\text{CO}$], 728 [$\text{M}^+ - 4\text{CO}$], 700 [$\text{M}^+ - 5\text{CO}$], 672

[$\text{M}^+ - 6\text{CO}$], 644 [$\text{M}^+ - 7\text{CO}$], 616 [$\text{M}^+ - 8\text{CO}$], 588 [$\text{M}^+ - 9\text{CO}$], 560 [$\text{M}^+ - 10\text{CO}$], 532 [$\text{M}^+ - 11\text{CO}$], 504 [$\text{M}^+ - 12\text{CO}$], 392 [$\text{M}^+ - (12\text{CO} + 2\text{Fe})$], 391 [$\text{M}^+ - (12\text{CO} + 2\text{Fe} + \text{H})$], 335 [$\text{M}^+ - (12\text{CO} + 3\text{Fe} + \text{H})$], 251 [$\text{M}^+ - (15\text{CO} + 3\text{Fe} + \text{H})$], 155 [$\text{M}^+ - (15\text{CO} + 3\text{Fe} + \text{Mo} + \text{H})$].

Results and Discussion

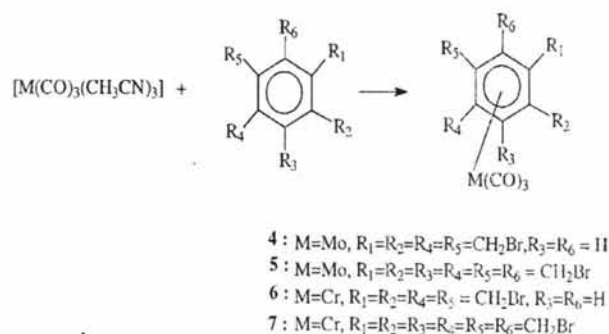
The reaction of $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ with 1,2,4,5-tetrakis(bromomethyl)benzene resulted in the isolation of $[\text{C}_6\text{H}_2(\text{CH}_2\text{Br})_4\text{Mo}(\text{CO})_3]$ (4) as a grey solid in 7.07% yield. This compound has been characterized by IR, ^1H NMR and mass spectroscopic data. The IR spectrum of compound 4 in cyclohexane exhibits two sharp $\nu(\text{CO})$ band at 1950 and 1987 cm^{-1} . These bands are regarded as terminal⁹ carbonyl stretching frequencies. This spectral pattern is characteristic of a complex in which $[\text{M}(\text{CO})_3]$ moiety is attached to an arene ligand¹⁰. The complex 4, in which 1,2,4,5-tetrakis(bromomethyl)benzene is bonded to the $[\text{Mo}(\text{CO})_3]$ moiety through the aromatic ring, as a whole has pseudo C_{3v} symmetry. This observation is consistent with the fact that substituted or unsubstituted benzene metal carbonyl complexes of group VI B show two IR-active stretching vibrations for the terminal carbonyl groups. For example, the complexes $[(p\text{-xyl})\text{Mo}(\text{CO})_3]$, $[\text{C}_6(\text{CH}_3)_6\text{Mo}(\text{CO})_3]$, $[(\text{DMA})\text{Mo}(\text{CO})_3]$, $[(\text{TMA})\text{Mo}(\text{CO})_3]$ all exhibit two ν_{CO} bands¹¹. The mode of attachment of ligand is indicated by IR spectrum has also been confirmed by ^1H NMR and mass spectral data. The ^1H NMR spectrum of 4 in CDCl_3 showed peaks at δ 4.58 (s, 8H) and δ 7.35 (s, 2H). The singlet at 4.58 suggests the presence of magnetically equivalent methylene protons of the type $\text{CH}_2\text{-X}$ where X indicates halogen atoms. The higher δ value is due to the anisotropic effect of aromatic system. The sharp singlet at δ 7.35 accounts for the presence of aromatic protons. The mass spectrum of 4 did not exhibit the expected molecular ion peak at m/z 630; instead, it showed peaks at 450 arising due to rapid loss of 3CO units and one Mo atom from molecular ion peak (M^+). The successive loss of 3CO units from parent molecular ion peak indicates the presence of $[\text{Mo}(\text{CO})_3]$ moiety in the complex. Other important peaks are observed at 370, 290, 210 and 130, which are due to sequential loss of four Br atoms. The number of significant isotopic peaks and their intensity in the spectrum are similar to those in the spectrum of the compound containing four bromine atoms, suggesting the presence of the four CH_2Br moi-

eties in the synthesized compound. The peaks at 80 and 96 are due to Br and Mo atoms respectively. Thus, on the basis of above arguments and spectral evidences the structure of the compound **4** is proposed as shown in Scheme II.

The reaction of *tris*(acetonitrile)molybdenumtricarboxyl $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ with 1,2,3,4,5,6-*hexakis*(bromomethyl)benzene resulted in the isolation of a grey solid compound $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Mo}(\text{CO})_3]$ (**5**) in 9.84% yield. The IR spectrum of **5** in cyclohexane exhibited two sharp $\nu(\text{CO})$ bands at 1952 and 1987 cm^{-1} . The bands are regarded as terminal⁹ carbonyl stretching frequencies. The spectral pattern is characteristic of a complex in which $[\text{M}(\text{CO})_3]$ moiety is attached to an arene ligand¹⁰. The complex **5**, in which 1,2,3,4,5,6-*tetrakis*(bromomethyl)benzene is bonded to $[\text{Mo}(\text{CO})_3]$ moiety through the aromatic ring, as a whole has pseudo C_{3v} symmetry and fits the 18-electron rule. This observation is consistent with the fact that substituted or unsubstituted benzene-metaltricarboxyl complexes show two IR-active stretching vibrations for the terminal carbonyl groups¹¹. In view of the close similarity of its IR spectrum with that of $[\text{C}_6\text{H}_2(\text{CH}_2\text{Br})_4\text{Mo}(\text{CO})_3]$ (**4**) we would like to formulate the complex as $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Mo}(\text{CO})_3]$ (**5**) in which the ligand donates σ -electrons to the metal so that the compound satisfies the 18-electron rule. On the basis of the above IR evidences we believe that the compound $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Mo}(\text{CO})_3]$ has the structure as shown in Scheme-II.

The reaction of $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ with 1,2,4,5-*tetrakis*(bromomethyl)benzene resulted in the isolation of $[\text{C}_6\text{H}_2(\text{CH}_2\text{Br})_4\text{Cr}(\text{CO})_3]$ (**6**) as a greenish-yellow solid in 12% yield. IR spectrum of **6** in cyclohexane exhibited two sharp $\nu(\text{CO})$ bands at 1925 and 1950 cm^{-1} . The bands are regarded as terminal⁹ carbonyl stretching frequencies. The spectral pattern is characteristic of a complex in which $[\text{M}(\text{CO})_3]$ moiety is attached to an arene ligand¹⁰. In complex **6**, 1,2,4,5-*tetrakis*(bromomethyl)benzene is bonded to $[\text{Cr}(\text{CO})_3]$ moiety through the aromatic ring. The $\nu(\text{CO})$ bands are similar to those reported for the related compounds, $[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Cr}(\text{CO})_3]$ ¹², $[(\text{C}_6\text{H}_5)_3\text{Cr}(\text{CO})_3]$ ¹³, $[(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)_3\text{Cr}(\text{CO})_3]$ ¹⁴ and $[(\text{C}_6\text{H}_5\text{CHO})\text{Cr}(\text{CO})_3]$ ¹⁵. The mode of attachment of the organic ligand is thus indicated by IR spectrum.

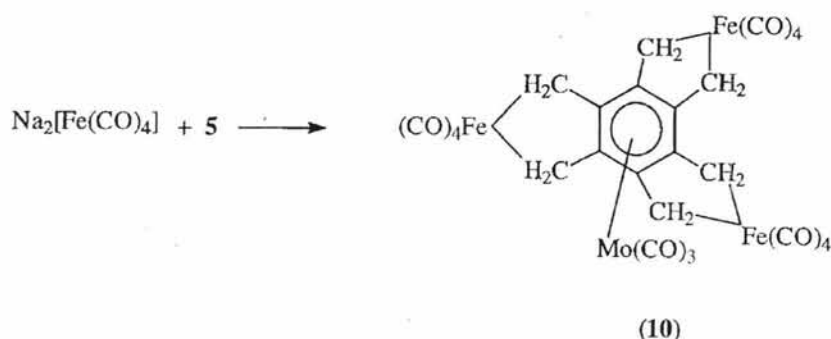
The mass spectrum of **6** exhibits the expected molecular ion peak at m/z 586, formed by initial ionization,



Scheme - II

which fits the molecular formula $[\text{C}_{13}\text{H}_{10}\text{O}_3\text{Br}_4\text{Cr}]$. The peaks at m/z 558, 530, 502 and 450 are due to the successive loss of three CO groups and Cr from M^+ which are responsible for the presence of $[\text{Cr}(\text{CO})_3]$ moiety in the complex¹⁶. Other peaks at m/z 370, 290, 210 and 130 are due to loss of four Br atoms. This type of peaks and their intensities suggest the presence of four $-\text{CH}_2\text{Br}$ moieties in the synthesized compound. The peaks at m/z 79 and 81 are due to the isotopic pattern peaks of Br. Therefore, on the basis of above arguments and spectral evidences the structure of the complex **6** is proposed as shown in Scheme-II.

The reaction of $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ with 1,2,3,4,5,6-*hexakis*(bromomethyl)benzene resulted in the isolation of a greenish compound $[\text{C}_6(\text{CH}_2\text{Br})_6\text{Cr}(\text{CO})_3]$ (**7**) in 16.74% yield. IR spectrum of **7** in cyclohexane exhibited two sharp $\nu(\text{CO})$ bands at 1925 and 1950 cm^{-1} . The bands are regarded as terminal⁹ carbonyl stretching frequencies. The spectral pattern is characteristic of a complex in which $[\text{M}(\text{CO})_3]$ moiety is attached to an arene ligand¹⁰. The ^1H NMR spectrum of **7** in CDCl_3 showed peaks at δ 2.16 (s, 12H). The high field singlet at δ 2.16 (s, 12H) suggests the presence of magnetically equivalent methylene protons of the type $-\text{CH}_2-\text{X}$ where X indicates halogen atoms. This δ -value is due to the anisotropic effect of aromatic system. There is no peak for aromatic protons. The mass spectrum of **7** did not exhibit the expected molecular ion peak at m/z 772; instead, it showed a peak at 236 arising due to rapid loss of six Br and two CO units from the molecular ion peak (M^+). The peak at 207 is due to loss of $(\text{CO} + \text{H})$ unit from the peak at 236. The peaks at 52 and 80 are due to Cr and Br atoms respectively. The successive loss of 3CO units and the isolated peak at 52 indicate the presence of $[\text{Cr}(\text{CO})_3]$ moiety in the complex¹⁶. The peaks at m/z 79 and 81 are the isotopic pattern peaks of Br. Therefore,



Scheme IV

clear indication of formation of neutral complex. Also, the exhibited peaks at 2035 to 1989 cm^{-1} are characteristic of the $[\text{Fe}(\text{CO})_4]$ moiety attached to the organic ligand¹⁰. On the other hand, the bands at 1931 and 1948 cm^{-1} are regarded as terminal carbonyl stretching frequencies. The spectral pattern is characteristic of a complex in which $[\text{Mo}(\text{CO})_3]$ moiety is attached to an arene ligand¹⁰.

The ^1H NMR spectrum of **10** in CDCl_3 exhibited a peak at δ 1.26 (12H). The high field singlet at δ 1.26 accounts for the presence of methylene protons which are magnetically equivalent. This up-field shift of methylene protons (δ 1.26) of **10** compared to that of the uncomplexed parent compound **5** clearly indicates the formation of Fe-C σ -bonds via methylene carbon atoms. Therefore, ^1H NMR spectrum shows that $[\text{Fe}(\text{CO})_4]$ moiety is attached through methylene carbon atoms of the organic ligands. The mass spectrum of **10** showed the molecular ion peak (M^+) at m/z 840, by initial ionization, which favourably fits the molecular formula $[\text{C}_{27}\text{H}_{12}\text{O}_{15}\text{Fe}_3\text{Mo}]$. The peaks at m/z 812, 784, 756, 728, 700, 672, 644, 612, 588, 560, 532, 504 and 392 are due to the sequential loss of 12 CO units and two Fe from the molecular ion peak (M^+). The peak at 391 is responsible for loss of one proton from the peak at 392. This fragmentation pattern is characteristic of metal-carbonyl organometallic complexes¹⁸ formed by coordination of $[\text{Fe}(\text{CO})_4]$ moiety through σ -bonds with the ligand. No isotopic pattern peaks characteristic of Br atom are observed, but the peak at m/z 168 for $[\text{Fe}(\text{CO})_4]$ is observed, which confirms that all the bromine atoms have been replaced by $[\text{Fe}(\text{CO})_4]$.

Other important peaks at 307, 279, 251 and 155 arising due to the successive loss of three CO groups and an Mo from the species corresponding to the peak at m/z 391 indicating the presence of $[\text{Mo}(\text{CO})_3]$ moiety in the complex. The peak at m/z 154 is due to loss of one proton from the species corresponding to the peak at m/z 155. The peaks at m/z 96 and 57 are due to the Mo and Fe atoms respectively. Thus, on the basis of above discussion and spectroscopic evidences the structure of the complex **10** is proposed as shown in Scheme-IV.

The formation of the multinuclear complexes **8**, **9** and **10** clearly indicates that it is possible to dehalogenate the precursor complexes **4**, **6** and **5** with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ and subject the resulting moiety to further metallation. Dehalogenation itself proceeds stepwise as has been demonstrated in the case of the reaction between $\text{Na}_2[\text{Fe}(\text{CO})_4]$ and 2,3-bis(bromomethyl)quinoxaline¹⁹. It is not clear whether the presence of $[\text{M}(\text{CO})_3]$ [$M = \text{Mo}, \text{Cr}$] bonded to the ring π -electrons should have an effect on facilitating the removal of bromine atoms from the methylene groups. But it is known that $\text{M}(\text{CO})_3$, ($M = \text{Mo}$) coordination generally increases the electron density at the ring site, which in turn should offset the carbonium character of methylene carbon. Consequently, some decrease in the susceptibility of nucleophilic attack should be expected. Further work on the comparative kinetics should clear this issue.

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