ISONITRILE DERIVATIVES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN CARBONYLS
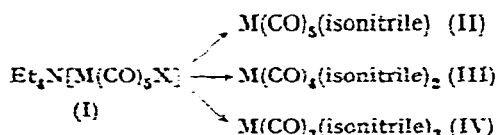
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During recent years mixed isonitrile carbonyl complexes of the Group VIA metals have been obtained either directly, by reaction of isonitriles with the metal hexacarbonyls[1,2] or indirectly, by reaction of amine[3] or olefin[4] complexes of the metal carbonyls with isonitriles. These methods have certain limitations. The direct method is limited to certain aryl isonitriles, because of the instability of the alkyl and some aryl isonitriles at temperatures necessary to effect reaction[1,2]. The indirect method has been employed almost exclusively with tris-amine-, or trienetricarbonylmetals, to obtain tris(isonitrile)tricarbonylmetals[3,4].

The present work describes a further indirect route to mixed isonitrile carbonyl derivatives of the Group VIA metals, which enables the mono-, bis-, and tris-isonitrile derivatives of both alkyl and aryl isonitriles to be prepared. Reaction of the tetra-ethylammonium salts of the halopentacarbonylmetal anions (I, M = Cr, Mo, or W; X = Cl, Br, or I) at 20–45° with either alkyl or aryl isonitriles gives mixtures of the mono(isonitrile)pentacarbonylmetals (II), the bis(isonitrile)tetracarbonylmetals (III) and the tris(isonitrile)tricarbonylmetals (IV) the relative amounts of which can be conveniently predetermined by choice of reactants and reaction conditions.

$$Et_4N[M(CO)_5X] \longrightarrow \begin{array}{l} M(CO)_5(isonitrile) \quad (II) \\ M(CO)_4(isonitrile)_2 \quad (III) \\ M(CO)_3(isonitrile)_3 \quad (IV) \end{array}$$

(I)

Most of the products obtained have not been previously reported. The mono-(alkylisonitrile)pentacarbonylmetals and the bis(alkyl- or -arylisonitrile)tetra-carbonylmetals are the first complexes of their type to be isolated. They have been characterised by analytical, infrared and representative molecular weight data. They can be separated by fractional crystallisation and sublimation. Combined yields are almost theoretical. All the products have sharp melting points.

The mono(isonitrile)pentacarbonylmetals are pale yellow (phenyl) to colourless (cyclohexyl) crystalline solids, which are extremely soluble in organic solvents and which can be sublimed at 40–60°/0.1 mm. They are air stable both in the solid state and in solution.

The bis(isonitrile)tetracarbonylmetals are normally slightly darker than the corresponding mono-derivatives, being pale yellow crystalline solids also stable to air. The possibility of *cis*- and *trans*-isomers arises, but in all the cases studied, the only

product obtained was the *cis*-isomer as determined by infrared spectroscopy (*vide infra*).

An attempt to convert the *cis*- to *trans*- by heating in solution resulted only in disproportionation to give mono- and tris-products, but only under drastic conditions (130–150°).

The tris-isonitrile complexes are yellow air-stable crystalline solids with properties similar to analogous compounds previously reported[3,4].

DISCUSSION

Mechanism of the reaction

In the direct thermal reaction of the metal hexacarbonyls with arylisonitriles the bis(isonitrile)tetracarbonylmetals were obtained at temperatures over 100° (ref. 2). Hence it was obvious that the bis- and tris-isonitrile derivatives found in the above reactions were not formed by further reaction of the initially formed mono(isonitrile)-pentacarbonyl metals, since the reactions were carried out at 20–40°. This was completely verified by allowing the mono-isonitrile complexes to stand in solution with a large excess of isonitrile for several days. No bis-isonitrile complex was formed. Similarly the tris-complexes could not be obtained from the bis-derivatives. Hence the products must be formed by different reaction mechanisms. The proposed reaction scheme is outlined below:
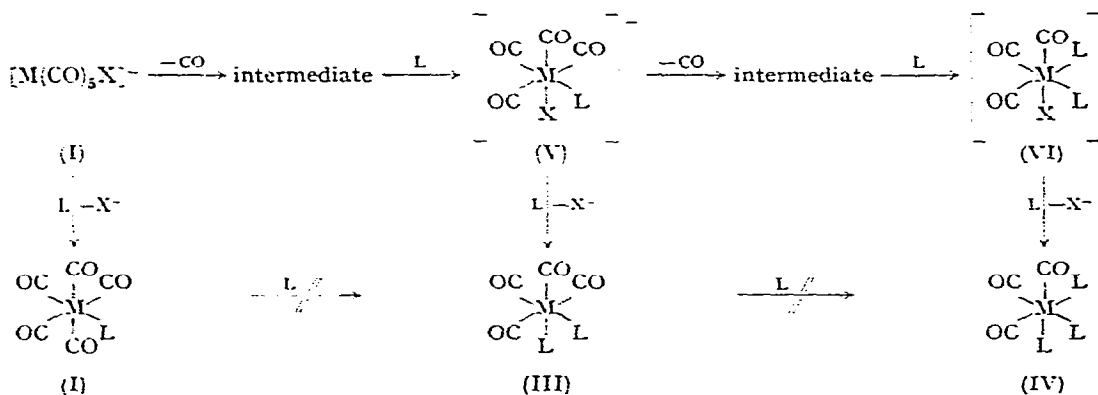
That this is essentially correct was demonstrated in part by the isolation of the orange crystalline intermediates (V, M = W, X = Cl, L = cyclohexyl and phenylisonitrile). The corresponding complexes with M = Mo or Cr could not be isolated the reaction proceeding too rapidly to completion. However, an intermediate orange coloration was observed in these reactions.

Further, in the reaction with phenyl isonitrile, with the chloropentacarbonyl-tungsten anion a second intermediate was isolated. This contained the tetraethyl-ammonium cation and isonitrile, and the analytical figures and infrared data (*vide infra*) are not inconsistent with its formulation as tetraethylammonium chlorobis-(phenylisonitrile)tricarbonyltungsten (VI, M = W, L = phenyl isonitrile, X = Cl). The compound gave *only* tris(phenylisonitrile)tricarbonyltungsten on further

reaction with isonitrile. In the absence of isonitrile, a disproportionation occurs, especially in chlorinated solvents, and the tris(phenylisonitrile)tricarbonyltungsten and the intermediate tetraethylammonium chloro(phenylisonitrile)tetracarbonyltungsten are formed as the major products together with tetraethylammonium chloride. Small amounts of unidentified decomposition products are also formed.

It is believed that the mono-isonitrile pentacarbonyls (II) are formed by direct attack of the isonitrile on the halopentacarbonyl metal anions by an S_N2 type displacement of halide. This view is substantiated by concentration and salt effects as will be seen later. A consideration of the mechanism of formation of the intermediates (V) and (VI) indicates a dissociative process by analogy with the reactions of the pentacarbonyl manganese halides. For these compounds both isotopic exchange of carbon monoxide[5] and displacement of carbon monoxide by isonitrile, phosphines, etc.[6] proceed by a dissociative elimination of the carbon monoxide.

Further, for the d^6-systems $Fe(CO)_4X_2$ and $Mn(CO)_5X$ the exchange of CO occurs by S_N2 and S_N1 mechanisms respectively. The change in mechanism is attributed to the decreased positive charge on the central atom[5]. Hence it is probable for the d^6-system $[M(CO)_5X]^-$ (M = Cr, Mo, W), in which the charge on the central atom is even lower, that formation of (V) from (I) will occur by a dissociative mechanism with elimination of a CO cis to the halogen as shown. The intermediate (V) can then react further with elimination of halide ion to give the bis(isonitrile)tetracarbonylmetals (III) or, by a further elimination of CO, give (VI). That CO elimination will again be a dissociative process follows from arguments similar to the above and is in agreement with the dissociative displacement of CO from monosubstituted manganese tetracarbonyl halides[7]. Elimination of halide from (VI) will give the tris(isonitrile) tricarbonylmetals (IV). It can be expected that the increasing negative charge from (I) → (V) → (VI) introduced by replacing CO by isonitrile will enhance the possibility of S_N1 type displacement of X^- for these complexes.

That these essentially are the reaction mechanisms was substantiated by variation of the reactants and reaction conditions as follows.

Changes in anion. It has been shown[5] that the rate of CO replacement in $Mn(CO)_5X$ is very dependent on X, being some 200 times more rapid for Cl than I. Hence assuming that the proposed reaction schemes are correct, it can be expected that a change from iodo- to chloro-pentacarbonylmetal anion should cause a large increase in the rate of formation of bis- and tris-products, and a slight increase in the rate of formation of mono-product[8], the overall effect being to favour the former. This is found experimentally. For reactions carried out in tetrahydrofuran the iodopentacarbonylmetal anions give only mono- and bis-derivatives, with the former predominating. However, the chloropentacarbonylmetal anions give almost no monoproduct, the products being mainly the bis- and the tris-products. The differences in ratios of reaction products from the different metals are small. In the limited number of reactions of the bromopentacarbonylmetal anions studied, the reaction products were intermediate, the bis-product being formed in high yield together with traces only of tris-product.

Isonitrile concentration. For an S_N2 type reaction the formation of the mono-isonitrile derivatives from (I) should be dependent on the concentration of isonitrile, the rate increasing for increasing concentration. The formation of bis- and tris-products may also be influenced in the same direction, in the formation step from the inter-

mediates (V) and (VI) respectively. However, the initial formation of these intermediates should be independent of ligand concentration and hence the overall effect should be an enhancement of mono(isonitrile)pentacarbonylmetals with increasing isonitrile concentration. This is observed.

Atmospheric conditions. It can be expected also that CO pressure will inhibit the formation of (V) and hence favour mono-substitution. This has been verified.

Salt effects. The effect of the presence of halide ion on the reactions was also studied. Addition of iodide to the reaction of the iodopentacarbonylmolybdenum anion with cyclohexyl isonitrile produced a small but significant decrease in the ratio of mono- to bis-substituted products formed. That the effect was small favours an S_N2 elimination of halide as proposed, and that more bis- is found can be expected since both the formation of the mono-product and the formation of the bis-product from (V) will be slightly slowed by the salt effect, while the formation of (V) from (I) should be unaffected.

Solvent effect. The effect of solvent on the reactions has not been studied extensively. However, it was observed that, for the reaction of the tetraethylammonium iodopentacarbonylmolybdenum with cyclohexyl isonitrile, the ratio of mono- to bis-substitution products varies with solvent. Thus for tetrahydrofuran ($\varepsilon = 7.6$) and especially diglyme ($\varepsilon = 5.7$) solvents which are known to facilitate the elimination of CO from the hexacarbonylmetals[9], the ratio mono- to bis- is much smaller than for chloroform ($\varepsilon = 4.8$), methylene chloride ($\varepsilon = 9$), or nitromethane ($\varepsilon = 34$). The similarity of the ratio for the three latter solvents in spite of very different dielectric constants (in parentheses) would appear to indicate a specific solvent effect enhancing formation of the bis-product for the former solvents. It was also noted that the reactions were markedly faster in methylene chloride, nitromethane and chloroform.

Change of metal. As has been mentioned, the variation in the ratios of reaction products vary very little but irregularly with change in the metal, and no attempts were made to correlate the results.

Change of isonitrile. It was also noticed that for the reactions of the iodopentacarbonylmetal anions, there is little difference in the product ratios for cyclohexyl and phenyl isonitriles, but that in the reactions of the corresponding chloro complexes the formation of the tris(isonitrile)tricarbonylmetals is favoured with the phenyl isonitrile.

The above effects are of value experimentally, in that mono-, bis-, or tris-substitution can be made to predominate in the reaction mixture by variation of the concentration and nature of the reactants.
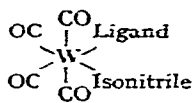
Thus reaction of the tetraethylammonium iodopentacarbonylmolybdenum in methylene chloride, with a large excess of cyclohexyl isonitrile under CO pressure gave virtually exclusively the mono(cyclohexylisonitrile)pentacarbonylmolybdenum. The effects for optimum yields of a specific substitution product are summarised in Table 1.

The isolation of the intermediates (V, M = W, X = Cl and L = phenyl or cyclohexyl isonitrile) also offers a unique possibility of preparing mixed bis- and tris-substituted derivatives of tungsten carbonyl of types (VII) and (VIII) (ligand = isonitrile, amine, phosphine, etc.). The complexes react at $45°$ with isonitrile to give mixtures of bis- and tris-isonitrile derivatives identical with those described.
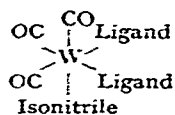
TABLE 1

REACTION CONDITIONS FOR SPECIFIC PRODUCT

Product required	Reactant	Solvent	Atmosphere	Isonitrile concentration
Mono-	$[M(CO)_5I]^-$	CH_2Cl_2	CO press	High
Bis-	$[M(CO)_5Br]^-$	THF, diglyme	Vacuum	Low
Tris-	$[M(CO)_5Cl]^-$	THF, diglyme	Vacuum	Low

$$
\begin{array}{c}
\text{OC} \quad \overset{\displaystyle CO}{\underset{\displaystyle }{|}} \text{Ligand} \\
\text{>W<} \\
\text{OC} \quad \underset{\displaystyle CO}{\overset{\displaystyle |}{}} \text{Isonitrile}
\end{array}
\qquad
\begin{array}{c}
\text{OC} \quad \overset{\displaystyle CO}{\underset{\displaystyle }{|}} \text{Ligand} \\
\text{>W<} \\
\text{OC} \quad | \quad \text{Ligand} \\
\text{Isonitrile}
\end{array}
$$

(VII)   (VIII)

Preliminary results indicate that the tetraethylammonium salts of the halo-pentacarbonylmetal anions also react in a fashion similar to that described above with amines, and phosphines.

Infrared spectra

A detailed infrared study of these complexes will be reported later. Only those points necessary to characterise the complexes will be discussed here.

The mono(isonitrile)pentacarbonylmetals and the tris(isonitrile)tricarbonyl-metals have spectra essentially similar to those reported by Cotton and Zingales for analogous complexes[4], confirming the structures and affirming that the tris-compounds have the *cis*-configuration (IV).

For the bis(isonitrile)tetracarbonylmetals, four infrared active CO stretching vibrations are observed. This is in agreement with a *cis*-configuration (III) (C_{2v}) for which four active bands can be predicted[10]. The spectra are similar to those reported[2] for *cis*-bis(phenylisonitrile)tetracarbonylmolybdenum, and to those of *cis*-bis(amine)-[11] and *cis*-bis(phosphine)tetracarbonylmetals[12,13]. That small amounts of the *trans*-products are present would seem unlikely, since the spectra are similar for each metal, and more important, are invariant with temperature. The spectra of bis(cyclohexylisonitrile)tetracarbonylmolybdenum and corresponding chromium complex were run at various temperatures up to 70° without any noticeable change in relative intensities.

The infrared spectra of the tetraethylammonium chloro(isonitrile)tetracarbonyl-tungsten complexes (V, M = W, L = isonitrile, X = Cl) in the region of the CN and CO stretching vibration are very similar to the *cis*-bis(isonitrile)tetracarbonylmetal complexes described above but with shifts in all the bands to lower frequencies. This agrees with the *cis*-configuration as in (V). As expected only one CN stretching vibration is observed. The bands are shown in table 2.

Because of the instability of the tetraethylammonium chlorobis(phenylisonitrile)-tricarbonyltungsten (VI, M = W, X = Cl, L = phenyl isonitrile) in solution, spectra were recorded only in nujol mulls. Two isonitrile bands were observed at 2120 and 2075 cm^{-1} together with three CO stretching vibrations at 1912 (vs), 1860 (m) and 1780 (s) cm^{-1}. The spectrum is reasonably consistent with the proposed formulation.

TABLE 2

INFRARED SPECTRA

Complex (I)	CH_2Cl_2		THF	
	ν_{CN}	ν_{CO}	ν_{CN}	ν_{CO}
M = W, X = Cl, L = phenyl isonitrile	2112	1996 s. dbt	2100	1978 m
		1891 vs		1887 vs
		1875 sh		~ 1878 sh
		1837 s		1826 s
M = W, X = Cl, L = cyclohexyl isonitrile	2146	1999 m	2138	1993 m
		1885 vs		1879 vs
		1864 sh		~ 1867 sh
		1806 s		1837 s

EXPERIMENTAL

All reactions were carried out under an atmosphere of pure nitrogen unless otherwise stated. Crystallisations were, however, effected in air. The infrared spectra were recorded on grating-spectrometers Perkin–Elmer models 521 and 337. Micro-analyses are by Dr. K. EDER, Ecole de Chimie, Geneva. All melting points are corrected.

Since the procedure used was essentially the same for the preparation of all products, general methods only will be described.

Mono- and bis-isonitrile complexes

To a solution of the tetraethylammonium iodopentacarbonylmetal[14] (4 mMole) in tetrahydrofuran (75 ml) was added the isonitrile (5.8 mMole) and the mixture was stirred at room temperature (Cr, Mo) or at 45° (W) with 1 metre water vacuum until reaction was complete (normally 3–5 h). This was ascertained by observing the disappearance of the band of the starting complex in the carbonyl region of the infrared at ~ 2060 cm^{-1}. The mixture was then filtered, and the solvent removed under reduced pressure. The residual solid was triturated with a minimum of petroleum ether, eliminating the mono-substituted product together with some of the bis-product. The residue was crystallised from methylene chloride–petroleum ether to give the bis-(isonitrile)tetracarbonylmetal. The petroleum ether fraction was evaporated to dryness and the mono(isonitrile)pentacarbonylmetal was then purified by sublimation at 60°/0.1 mm, (Mo, W) or 45°/0.1 mm (Cr). Traces of hexacarbonylmetal were readily eliminated from the sublimed mono(isonitrile)pentacarbonylmetals by dissolving the mixture in petroleum ether and evaporating the solution at 12 mm. The hexacarbonylmetals are eliminated with the solvent. The residue of sublimation contained almost pure bis-product which could be recovered and recrystallised as described above. In all of the reactions carried out as above the ratio of mono- to bis- was approximately 2:1 with small variations from chromium to tungsten and cyclohexyl to phenyl isonitrile. The above conditions will be referred to as standard.

Bis- and tris-isonitrile complexes

A mixture of these complexes, together with very small amounts of the mono-products are obtained when the corresponding chloropentacarbonyl anions[12] (Mo or

Cr only) are used in the above reaction. To a solution of the tetraethylammonium chloropentacarbonylmetal anion (Cr or Mo) (5 mMol) in THF (150 ml) was added the isonitrile (12 mMol) and the mixture stirred at room temperature until reaction was complete as defined above. Filtration and evaporation of the solvent gave a solid residue from which the traces of mono-product were removed by trituration with pet. ether. The bis- and tris-products were then separated by fractional crystallisation from methylene chloride–pet. ether, the tris-product being less soluble for phenyl isonitrile derivatives, and more soluble for cyclohexyl isonitrile derivatives. This separation was more difficult than the corresponding separation of mono- and bis-products, and was rarely quantitative. For the reactions with cyclohexyl isonitrile the ratio of bis- to tris- was found of the order 1:1, while for phenyl isonitrile the ratio was 1:3 with small variations from chromium to molybdenum using the above conditions.

An alternative method of preparing the bis(isonitrile)tetracarbonyls consists of carrying out the above reaction using the bromopentacarbonylmetal anions in the same proportions. In this case, the amount of bis- to tris-product in the mixture is greatly enhanced. The separation is as above.

Reactions of $Et_4N[W(CO)_5Cl]$ with isonitriles

Since these reactions differ from the general reaction described, a detailed experimental is given.

Cyclohexyl isonitrile. The reaction was carried out with quantities as above. However, on completion of the reaction, determined as described, the mixture was filtered and a large volume of petroleum ether added. The precipitated solid was then crystallised from tetrahydrofuran–pet. ether giving tetraethylammonium chloro-(cyclohexylisonitrile)tetracarbonyltungsten as an orange solid, in 55–60 % yield. The mother liquors of the reaction could be shown to contain bis- and tris-isonitrile derivatives but these were neglected.

If the reaction was carried out at 45°, instead of at room temperature, the reaction proceeded smoothly, to the normal reaction mixture of mono-, bis- and tris-products, which were separated as described for the corresponding chromium and molybdenum reactions above.

Similarly, reaction of the isolated tetraethylammonium chloro(cyclohexyl-isonitrile)tetracarbonyltungsten with cyclohexyl isonitrile in tetrahydrofuran at 45° gave a mixture of bis- and tris-isonitrile derivatives (no mono- as expected).

Phenyl isonitrile. Reaction as above at room temperature with phenyl isonitrile resulted in immediate deepening of the colour of the reaction solution from yellow to dark orange. During this reaction the tetraethylammonium chlorobis(phenyl-isonitrile)tricarbonyltungsten was precipitated as a deep red-orange solid. This was filtered off, washed with water, and tetrahydrofuran (minimum) and then dried. Attempted recrystallisations were invariably unsuccessful because of disproportionation of the material in solution (*vide infra*). Further reaction of the material, with phenyl isonitrile in nitromethane at 45° gave tetraethylammonium chloride, and tris(phenylisonitrile)tricarbonyltungsten as the sole products. When the material was dissolved in methylene chloride without isonitrile, the colour gradually changed from red to yellow, and tetraethylammonium chloride was precipitated. From the solution the tetraethylammonium chloro(phenylisonitrile)tetracarbonyltungsten was isolated by precipitation with petroleum ether and purified as below. The tris-

(phenylisonitrile)tricarbonyltungsten could be isolated from the mother liquors.

The filtrate of the initial reaction was treated with pet. ether and after crystallisation from tetrahydrofuran–pet. ether, the tetraethylammonium chloro(phenylisonitrile)tetracarbonyltungsten was obtained as a dark yellow solid in 50 % yield. Further reaction of this at 45° with phenyl isonitrile gave a mixture of bis- and tris-(isonitrile) derivatives separated as previously described.

Repetition of the initial reaction at 45° again afforded the insoluble material described above as a precipitate; however, no trace of the tetraethylammonium chloro-(phenylisonitrile)tetracarbonyltungsten was obtained the reaction proceeding to the bis- and tris-isonitrile derivatives which were separated as indicated previously.

The physical data for all the products described are given in Table 3.

Attempted conversion of mono- to bis-products

Mono(cyclohexylisonitrile)pentacarbonylmolybdenum was allowed to stand in tetrahydrofuran with a large excess of cyclohexylisonitrile. The infrared spectrum of the mixture (2200–1800 cm^{-1}) was unchanged after 48 h. No trace of the bis-product was observed.

Attempted conversion of bis- to tris-products

In a reaction similar to the above, bis(cyclohexylisonitrile)tetracarbonylmolybdenum was unreacted after 48 h in tetrahydrofuran with a large (10 molar) excess of the isonitrile. This was again determined spectroscopically.

Attempted conversion of bis-products

Solutions of bis(cyclohexylisonitrile)tetracarbonylmolybdenum and -chromium in heptane were prepared and the infrared spectra in the region 2200–1800 cm^{-1} were recorded. The solutions were then heated in the infrared cell to 50° and after maintaining this temperature for 1 h the spectra recorded at 50° were identical with those at room temperature. The process was repeated at 60° and 70° with the same results.

The molybdenum product was then heated in decalin to 130–150°. After 1 h there was evidence of the formation of both mono- and tris-products. The bands of these products in the infrared (2200–1800 cm^{-1}) are easily distinguished from those of the bis- and identified by reference to the pure materials. A control experiment run concurrently showed evidence of decomposition.

Factors affecting product ratios

(a) *Isonitrile concentrations.* Tetraethylammonium iodopentacarbonylmolybdenum was reacted with cyclohexyl isonitrile in tetrahydrofuran with an anion to solvent ratio as standard but with a ten-fold increase in isonitrile. Comparison of the infrared spectrum of this reaction with that of the corresponding standard reaction showed an increase in the mono-isonitrile compound present. This was confirmed by isolation of the mono-compound in 80 % yield (*cf.* ~ 65 %).

(b) *Atmospheric conditions.* The standard reactions were carried out with a slight (1 metre water) vacuum. On repeating the reaction with a slight (again 1 metre water) over-pressure of carbon monoxide, and controlling the reaction by infrared and also isolation of the mono-complex, an enhancement of this complex of the same magnitude as above (80 % isolated) was observed.

TABLE 3

PHYSICAL DATA OF THE PRODUCTS

Compound	M.p.	Calcd.					Found				
		C	H	M	N	Mol. wt.	C	H	M	N	Mol. wt.
(PhNC)Mo(CO)₅	74°	42.5	1.48	28.3	—	339	42.57	1.6	27.92	—	338
(PhNC)₂Mo(CO)₃	104°	52.19	2.43	23.17	6.77	414	52.08	2.3	22.96	6.81	414
(PhNC)₃Mo(CO)₃	141°	58.9	3.09			507	59.17	3.47			593
(C₆H₁₁NC)Mo(CO)₅	86°	41.75	3.21	27.8			41.9	3.34	27.9		
(C₆H₁₁NC)₂Mo(CO)₄	108°	50.71	5.20	24.5			50.5	5.26	22.3		
(C₆H₁₁NC)₃Mo(CO)₃	116°	56.8	6.56	18.91			57.4	6.47	19.12		
(PhNC)W(CO)₆	80°	33.75	1.18	43.07			34.00	1.46	42.88		
(PhNC)₂W(CO)₄	116°	43.04	2.02	36.63			42.75	2.37	36.97		
(PhNC)₃W(CO)₃	145-6°	49.92	2.62				50.26	2.66			
(C₆H₁₁NC)W(CO)₆	76°	33.27	2.56	42.78			33.43	2.78	44.36		
(C₆H₁₁NC)₂W(CO)₄	107°	42.94	4.31	35.78	5.45		41.81	4.48	35.58	5.66	
(C₆H₁₁NC)₃W(CO)₃	121°	48.40	5.59				48.96	5.64			
(PhNC)Cr(CO)₅	55-6°	48.82	1.71				49.1	1.84			
(PhNC)₂Cr(CO)₄	87-8°	58.38	2.72	14.05			58.42	2.87	13.89		
(PhNC)₃Cr(CO)₃	108-9°	64.71	3.4	11.68	9.44		64.50	3.58	11.9	9.48	
(C₆H₁₁NC)Cr(CO)₅	49°	47.83	3.68	17.27			48.45	3.77	17.43		
(C₆H₁₁NC)₂Cr(CO)₄	95-6°	50.53	5.8				56.61	5.8			
(C₆H₁₁NC)₃Cr(CO)₃	97°	62.18	7.17				62.34	7.02			
Et₄N[(PhNC)W(CO)₄Cl]	88°	40.4	4.46	32.55			40.7	4.59	32.52		
Et₄N[(C₆H₁₁NC)W(CO)₄Cl]	67-8°	39.93	5.47	32.24			40.01	5.47	32.20		
Et₄N[(PhNC)₂W(CO)₃Cl]	134-5° (d)	46.92	4.73	28.74	6.57		47.12	5.09	28.1	6.54	

Note. Yields are not given since they vary with the reactants and reaction conditions. However, in general the total yield based on the halopenta-carbonyl anions was always almost theoretical. Some losses were incurred in the separation procedures.

Salt effect. Reaction of tetraethylammonium iodopentacarbonyl molybdenum with cyclohexyl isonitrile in tetrahydrofuran with the standard quantities but in presence of sufficient tetraethylammonium iodide to give a saturated solution, gave a reaction mixture which by infrared analysis showed a slight but definite enhancement of the bis-product over the standard reaction.

Solvent effects. The reaction of the tetraethylammonium iodopentacarbonyl-molybdenum with cyclohexyl isonitrile was carried out with standard quantities in a variety of solvents. In methylene chloride and nitromethane, both infrared analysis and isolation of the products shows a substantial increase in mono-product (> 90 % isolated) over the standard reaction (65 %) (in tetrahydrofuran). In diglyme the product ratio determined as above was lower than the standard reaction (50 % mono-).

Combined effects. By reacting tetraethylammonium iodopentacarbonylmolybdenum with cyclohexyl isonitrile (10 times standard) in methylene chloride under carbon monoxide pressure, a yield of mono(cyclohexylisonitrile)pentacarbonyl-molybdenum of 95 % was obtained.

ACKNOWLEDGEMENTS

SUMMARY

The reaction of the tetraethylammonium salts of the halopentacarbonyl anions of the Group VIA metals, with aryl and alkyl isonitriles affords mono-, bis-, and tris-isonitrile derivatives of the metal carbonyls in ratios which can be predetermined by suitable choice of reactants and reaction conditions. The mechanism is discussed.

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