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THE PREPARATION AND SYNTHETIC VALUE OF *fac*-$[M(CO)_3(NCR)_3]^+$ CATIONS (M = Mn or Re; R = Et, Pr OR $PhCH_2$)

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Abstract—Treatment of $MBr(CO)_5$ (M = Mn or Re) with $AgClO_4$ and an organonitrile in a suitable solvent affords the complexes *fac*-$[M(CO)_3(NCR)_3][ClO_4]$, (R = Et, Pr or $PhCH_2$). The use of these complexes as synthetic precursors has been illustrated by the preparation of *fac*-$[M(CO)_3L_3][ClO_4]$, (M = Mn, L = NH_3 or L_3 = dien; M = Re, L_3 = triphos). Pure *fac*-$[Re(CO)_3(NH_3)_3][ClO_4]$ could not be prepared using this nitrile displacement route, but may be isolated, as the PF_6^- salt, from the reaction of $[Re(CO)_3(toluene)][PF_6]$ and ammonia in chloroform.

In a recent publication[1] Kubas illustrated the use of the complexes *fac*-$W(CO)_3(NCR)_3$, (R = Et or Pr), as starting materials for the synthesis of several polyolefin- and phosphine-substituted tungsten carbonyls. These nitrile complexes were preferred to the commonly employed *fac*-$W(CO)_3(NCMe)_3$ because not only were they formed more rapidly than the acetonitrile complex from $W(CO)_6$ but they also possessed higher solubilities in solvents of synthetic utility. Subsequent nitrile substitution reactions could therefore be achieved more effectively. Kubas also suggested that the use of higher nitriles as ligands should be encouraged, rather few complexes containing these ligands having been explored.

We are therefore prompted to report the preparation, characterization and use of the complexes *fac*-$[M(CO)_3(NCR)_3][ClO_4]$ (M = Mn or Re; R = Et, Pr or $PhCH_2$), the rhenium cations with R = Et or Pr being isoelectronic and isostructural with *fac*-$W(CO)_3(NCR)_3$ reported by Kubas.[1]

EXPERIMENTAL

All reactions were performed under dry nitrogen using anhydrous, deoxygenated solvents. IR spectra were recorded using Perkin–Elmer 597 and 599B spectrometers. The ^1H NMR spectra were recorded as $CDCl_3$ solutions using a Jeol PS 100 spectrometer with tetramethylsilane as internal standard.

Preparation of fac-$[Mn(CO)_3(NCR)_3][ClO_4]$, (R = Et, Pr or $PhCH_2$)

A solution of $MnBr(CO)_5$ (0.55 g, 2.00 mmol), $AgClO_4$ (0.42 g, 2.03 mmol) and EtCN (0.36 g, 6.50 mmol) in 30 cm^3 of chloroform was refluxed for 5 hr. The AgBr formed was filtered off and the filtrate evaporated to low bulk. Addition of diethyl ether afforded an orange precipitate of $[Mn(CO)_3(NCEt)_3][ClO_4]$, (0.71 g, 88%; ^1H NMR in $CDCl_3$: δ, 1.43 (3), 2.86 (2)). Found: C, 35.1; H, 4.1; N, 10.6. $C_{12}H_{15}ClMnN_3O_7$ calc.: C, 35.7; H, 3.8; N, 10.4.

The PrCN complex was prepared in a similar fashion, except that PrCN (0.45 g, 6.50 mmol) was used with a reflux time of 16 hr. The product, isolated as a yellow oil which could not be induced to crystallize, was freed from excess PrCN by high vacuum pumping. Yield, 0.79 g (89%). ^1H NMR in $CDCl_3$: δ, 1.10 (3), 1.82 (2), 2.83 (2). Found: C, 39.2; H, 4.8; N, 9.2. $C_{15}H_{21}ClMnN_3O_7$ calc.: C, 40.4; H, 4.8; N, 9.4.

The $PhCH_2CN$ analogue was also prepared in the above manner as an orange oil using $PhCH_2CN$ (0.70 g, 6.00 mmol) and a reflux time of 4 hr. Yield, 0.91 g (77%). ^1H NMR in $CDCl_3$: δ, 4.23 (2), 7.33 (5). Found: C, 54.8; H, 3.5; N, 6.9. $C_{27}H_{21}ClMnN_3O_7$ calc.: C, 55.0; H, 3.6; N, 7.1.

Preparation of fac-$[Re(CO)_3(NCEt)_3][ClO_4]$. A mixture of $ReBr(CO)_5$ (1.00 g, 2.50 mmol), $AgClO_4$ (0.52 g, 2.51 mmol) and EtCN (25 cm^3) was refluxed for 16 hr. After removal of the AgBr, diethyl ether (70 cm^3) was added to the filtrate to give colourless crystals on standing. These were washed with diethyl ether and dried *in vacuo*. Yield, 0.86 g (65%). ^1H NMR in $CDCl_3$: δ, 1.44 (3),

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2.96 (2). Found: C, 26.8; H, 2.8; N, 7.9. $C_{12}H_{15}ClN_3O_7Re$ calc.: C, 26.9; H, 2.8; N, 7.9.

Preparation of fac-$[Re(CO)_3(NCCH_2Ph)_3][ClO_4]$. A mixture of $ReBr(CO)_5$ (0.50 g, 1.25 mmol), $AgClO_4$ (0.25 g, 1.21 mmol), $PhCH_2CN$ (0.43 g, 3.69 mmol) and di-isopropyl ether (20 cm^3) was refluxed for 20 hr. Decantation of the solvent left a brown solid which was partly soluble in 20 cm^3 of chloroform leaving a residue of AgBr. Removal of the chloroform left a viscous liquid which crystallized after standing for a few days at room temperature. Yield, 0.73 g (82%). ^1H NMR in $CDCl_3$: δ, 4.30 (2), 7.33 (5). Found: C, 44.6; H, 3.1; N, 5.6. $C_{27}H_{21}ClN_3O_7Re$ calc.: C, 45.0; H, 2.9; N, 5.8.

Preparation of fac-$[Mn(CO)_3(NH_3)_3][ClO_4]$. Ammonia gas was passed for 1 hr into solutions of *fac*-$[Mn(CO)_3(NCR)_3][ClO_4]$, (0.25 g; R = Et, Pr or $PhCH_2$) in 10 cm^3 of chloroform. The cream–yellow products were filtered, washed with chloroform and dried *in vacuo*. Yields at least 80%. Found: C, 12.5; H, 3.3; N, 14.5. $C_3H_9ClMnN_3O_7$ calc.: C, 12.5; H, 3.1; N, 14.5.

Preparation of fac-$[Mn(CO)_3(dien)][ClO_4]$. A mixture of *fac*-$[Mn(CO)_3(NCR)_3][ClO_4]$, (1.00 mmol; R = Et, Pr or $PhCH_2$), diethylenetriamine (0.11 g, 1.10 mmol) and chloroform (10 cm^3) was refluxed for 0.5 hr. The pale yellow products were filtered, washed with chloroform and dried *in vacuo*. Yields at least 90%. Found: C, 25.1; H, 3.9; N, 12.5. $C_7H_{13}ClMnN_3O_7$ calc.: C, 24.6; H, 3.8; N, 12.3.

Preparation of fac-$[Re(CO)_3(triphos)][ClO_4]$. A mixture of *fac*-$[Re(CO)_3(NCEt_3)][ClO_4]$, (0.26 g, 0.50 mmol), 1,1,1-tris(diphenylphosphinomethyl) ethane (0.34 g, 0.55 mmol) and acetone (20 cm^3) was refluxed for 2 hr. Removal of the acetone left a creamy–white residue which was redissolved in acetone, the solution filtered and the product precipitated by addition of light petroleum. Yield 0.32 g (65%). Found: C, 52.8; H, 3.9. $C_{44}H_{39}ClO_7P_3Re$ calc.: C, 53.1; H, 4.0.

Preparation of fac-$[Re(CO)_3(NH_3)_3][PF_6]$ *from* $[Re(CO)_3(\eta\text{-}C_6H_5Me)][PF_6]$. Ammonia gas was slowly passed for 6 hr through a suspension of $[Re(CO)_3(\eta\text{-}C_6H_5Me)][PF_6]$[2] (0.05 g) in chloroform (15 cm^3). The white solid produced was filtered, washed with diethyl ether and dried *in vacuo*. Yield, 0.038 g (82%). Found: C, 7.8; H, 2.0; N, 9.1. $C_3H_9F_6N_3O_3PRe$ calc.: C, 7.8; H, 1.9; N, 9.0.

RESULTS AND DISCUSSION

High yields of the complexes *fac*-$[M(CO)_3(NCR)_3][ClO_4]$, (M = Mn, R = Et, Pr or $PhCH_2$; M = Re, R = Et or $PhCH_2$) have been isolated from the reactions of $MBr(CO)_5$ with RCN in the presence of $AgClO_4$. This method has previously been employed for the syntheses of the acetonitrile analogues.[3,4] The *fac*-$[Mn(CO)_3(NCR)_3][ClO_4]$ (R = Pr or $PhCH_2$) complexes were isolated as non-crystallizable viscous oils. The related *fac*-$[Mn(CO)_3L_3][ClO_4]$ (L = acetone or tetrahydrofuran) complexes are also known as oils.[5] IR data for the nitrile complexes are presented in Table 1 and are, not unexpectedly, similar to those of the acetonitrile analogues.[4] Two ν(CO) bands ($A_1 + E$) are observed in the solution spectra, the lower frequency band being of greater half width. The presence of the T_2 ν(ClO) and δ(OClO) bands at *ca.* 1095 and *ca.* 625 cm^{-1} coupled with the absence of A_1 ν(ClO) bands at *ca.* 935 cm^{-1} are indicative of ionic perchlorate and an increase in ν(CN) from that of the free nitrile is typical of *N*-bonded nitrile. The ^1H NMR spectra are given in the Experimental section, the observation of a single set of resonances for each cation being further support for facial configurations.

As illustrations of the synthetic value of these nitrile complexes, we have prepared the complexes *fac*-$[M(CO)_3L_3][ClO_4]$ (M = Mn, L = NH_3 or L_3 = dien; M = Re, L_3 = triphos) in excellent yields by simple nitrile displacement reactions. Significant IR bands are listed in Table 1, *fac*-$[Re(CO)_3(triphos)][ClO_4]$ showing three ν(CO) bands rather than the expected two due to solid state E mode splitting. Although *fac*-$[Mn(CO)_3(NH_3)_3][ClO_4]$ has not been reported previously, the corresponding chloride has been prepared[6] by a high pressure reaction of $MnCl(CO)_5$ with anhydrous liquid ammonia, and the $[Mn(CO)_5]^-$ salt by photolysis of a solution of $Mn_2(CO)_{10}$ in the presence of ammonia.[7] Clearly the present route offers a simple alternative. The complex *fac*-$[Mn(CO)_3(triphos)][Mn(CO)_5]$ has been prepared[8] by a similar disproportionation of $Mn_2(CO)_{10}$ using triphos, but the analogous cation *fac*-$[Re(CO)_3(triphos)]^+$, isolated here as its perchlorate salt, appears not to have been reported before.

Surprisingly, in view of the simplicity of the above reactions, we were unable to obtain pure samples of *fac*-$[Re(CO)_3(NH_3)_3][ClO_4]$ from reactions of solutions of *fac*-$[Re(CO)_3(NCR)_3][ClO_4]$ with ammonia gas. However, *fac*-$[Re(CO)_3(NH_3)_3]$ $[PF_6]$ was successfully isolated by displacement of arene from $[Re(CO)_3(\eta\text{-}C_6H_5Me)][PF_6]$. The trisammine cation has previously been prepared as its chloride by high pressure reactions of either $Re_2(CO)_{10}$ or $Re(CO)_5H$ with a solution of ammonium chloride in liquid ammonia,[9] and as the phosphinate $R_2PO_2^-$ (R = Me or Ph) salts from

Table 1. IR frequencies (cm^{-1})[a]

Compound	$\nu(CO)$	$\nu(CN)^d$	$\nu(ClO)^d$	$\delta(OClO)^{d,f}$	$\nu(NH)^d$
$[Mn(CO)_3(NCEt)_3][ClO_4]$	2050, 1972^b	2293 w	1099 br	623	
$[Mn(CO)_3(NCPr)_3][ClO_4]$	2048, 1966^b	2290 w	1097 br	627	
$[Mn(CO)_3(NCCH_2Ph)_3][ClO_4]$	2045, 1965^b	2285 w	1092 br	625	
$[Re(CO)_3(NCEt)_3][ClO_4]$	2045, 1935^b	2297 w	1093 br	625	
$[Re(CO)_3(NCCH_2Ph)_3][ClO_4]$	2052, 1950^b	2300 w	1096 br	626	
$[Mn(CO)_3(NH_3)_3][ClO_4]$	2043, 1919^c		1096 br	627	3358 m, 3296 w
$[Mn(CO)_3(dien)][ClO_4]$	2035, 1923^c		1090 br	626	3340 m, 3298 m
$[Re(CO)_3(triphos)][ClO_4]$	2035, 1967, 1948^d		1098 br	626	
$[Re(CO)_3(NH_3)_3][PF_6]$	2028, 1902^b		840 br[e]	560[g]	3370 m, 3300 m

[a] All bands strong unless otherwise indicated. [b] $CHCl_3$ solution. [c] MeCN solution. [d] Nujol mull. [e] ν_3, PF_6^-. [f] Strong $\delta(MCO)$ bands also found between 700–600 cm^{-1}. [g] ν_4, PF_6^-.

$[Re(CO)_3(\mu\text{-}O_2PR_2)(THF)]_n$ and liquid ammonia.[10] Again the route suggested here represents an attractive alternative. The complex *fac*-$[Re(CO)_3(triphos)][PF_6]$ may also be prepared by a similar displacement reaction from $[Re(CO)_3(\eta\text{-}C_6H_5Me)][PF_6]$.

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