Gold(III) Complexes with Nitriles containing Aromatic Nuclei: Crystal and Molecular Structure of Trichloro(*p*-toluonitrile)gold(III)†

Wolfgang Hiller
Institut für Anorganische Chemie, Universität Tübingen, D-7400 Tübingen, Federal Republic of Germany
Daniela Belli Dell'Amico*
Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, I-56100 Pisa, Italy

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Anhydrous gold(III) chloride reacts with nitriles to give complexes of the type [$AuCl_3(NCR)$] (R = $C_6H_4CH_3$-*p*, $CH_2C_6H_5$, or C_6H_5), in spite of the ability of gold(III) chloride to metallate unsubstituted or methyl-substituted aromatic rings. An *X*-ray diffraction study of the *p*-toluonitrile derivative at 190 K confirmed that the product is a gold(III) end-on nitrile complex with gold in its usual square co-ordination. The product crystallizes in the monoclinic space group $P2_1/n$, with *a* = 6.669(2), *b* = 12.574(3), *c* = 13.740(3) Å, β = 90.30(2)°, and *Z* = 4. Refinement converged to *R* = 0.021 for 1 246 independent 'observed' reflections. The Au–Cl bond lengths are 2.236(2) and 2.284(2), 2.271(2) Å for the chlorine atom *trans* to the nitrile and for the *cis* chlorines, respectively; Au–N 1.980(6) Å. Complexes of formula $AuCl_2(NCR)$ (R = $C_6H_4CH_3$-*p* or $CH_2C_6H_5$), obtained with a large excess of the nitrile and over long reaction times, are suggested to be, on the basis of spectroscopic data, ionic mixed-valence species of the type [$AuCl_2(NCR)_2$][$AuCl_2$].

Gold(III) chloride as the anhydrous species or as the tetrachloroaurate(III) anion is very reactive. Typical reactions are: (i) co-ordinative additions with ligands yielding four-co-ordinate complexes [equation (1); L = pyridine,[1] CH_3CN,[1] azobenzene,[2,3] or dimethyl sulphoxide[4]], (ii) reductions to oxidation state I or to mixed-valence complexes [equations (2) and (3);

$$Au_2Cl_6 + 2L \longrightarrow 2[AuCl_3L] \quad (1)$$

$$Au_2Cl_6 + 4L \longrightarrow 2[AuClL] + 2Cl_2L \quad (2)$$

$$Au_2Cl_6 + 2L \longrightarrow [Au_2Cl_4L] + Cl_2L \quad (3)$$

$$Au_2Cl_6 + RH \longrightarrow [AuCl_2R] + HCl \quad (4)$$

L = CO,[1,5] PPh_3,[6] olefin,[7] RNC (R = C_6H_5, $C_6H_4OCH_3$-*p*, or $C_6H_4CH_3$-*p*),[8] or 1,4-thiazan-3-one[9]], and (iii) metallation of the aromatic ring[10] [equation (4); R = aryl]. Reactions (iii) appear to be inhibited by nitrogen-containing Lewis base functions on the arene.[2,3,11,12] In agreement with these new findings and contrary to an earlier report,[10b] organic nitriles containing aromatic rings react simply by type (i). We report here the reactions with benzonitrile, *p*-toluonitrile, and phenylacetonitrile and the crystal structure of the product obtained with *p*-toluonitrile. Under particular conditions, diamagnetic products which analyse as $AuCl_2(NCR)$ are obtained which are discussed herein. A preliminary account of this work was reported earlier.[12]

Experimental

All operations were carried out under a prepurified nitrogen atmosphere. Solvents were dried according to conventional methods. N.m.r. spectra were measured with JEOL PS100 and Varian ME360 instruments. I.r. spectra were measured with a Perkin-Elmer 283 instrument. Anhydrous gold(III) chloride was prepared according to the procedure previously described.[1]

Preparation of Complexes [$AuCl_3(NCR)$] (R = C_6H_5, $C_6H_4CH_3$-*p*, *or* $CH_2C_6H_5$).—Analogous results were obtained (*a*) in CH_2Cl_2 at solid CO_2 temperature, with the stoicheiometric amount of the nitrile; (*b*) in CH_2Cl_2 at room temperature, with the stoicheiometric amount of the nitrile; and (*c*) in the neat liquid nitrile at room temperature (in the case of *p*-toluonitrile some CH_2Cl_2 was added to dissolve the solid nitrile at room temperature). We describe some typical preparations.

[$AuCl_3(NCC_6H_5)$] [*Method* (*a*)]. A solution of benzonitrile (0.402 g, 3.90 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a suspension of anhydrous gold(III) chloride (1.266 g, 4.17 mmol) in CH_2Cl_2 (10 cm^3) at −78 °C. After stirring for 1 h, while allowing the temperature to rise to ambient, a yellow suspension was obtained. The product was filtered off, and dried *in vacuo* (47% yield) (Found: C, 20.8; H, 1.3; Cl, 25.8, N, 3.7. Calc. for $C_7H_5AuCl_3N$: C, 20.7; H, 1.2; Cl, 26.2; N, 3.4%).

[$AuCl_3(NCC_6H_4CH_3$-*p*)] [*Method* (*b*)]. A solution of *p*-toluonitrile (1.37 g, 11.72 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a suspension of anhydrous gold(III) chloride (3.10 g, 10.22 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. After stirring for 2 h, the yellow suspension obtained was concentrated to *ca.* 10 cm^3 and n-heptane (20 cm^3) added. The final suspension was filtered and the yellow product dried *in vacuo* (77% yield) [Found: C, 22.8; H, 1.8; Cl, 25.5; N, 3.1%; *M* (cryoscopy in nitrobenzene), 434. Calc. for $C_8H_7AuCl_3N$: C, 22.8; H, 1.7; Cl, 25.3; N, 3.3%; *M*, 420.5].

[$AuCl_3(NCCH_2C_6H_5)$] [*Method* (*c*)]. Anhydrous gold(III) chloride (2.164 g, 7.13 mmol) was added to neat phenylacetonitrile (5 cm^3, 5.08 g, 43.35 mmol) at room temperature. After stirring for 1 h a yellow suspension was obtained. After addition of CCl_4 (20 cm^3) the yellow product was filtered off and dried *in vacuo* (67% yield) (Found: C, 23.4; H, 1.8; Cl, 24.7; N, 3.5. Calc. for $C_8H_7AuCl_3N$: C, 22.8; H, 1.7; Cl, 25.3; N, 3.3%).

Reaction between [$AuCl_3(NCC_6H_4CH_3$-*p*)] *and Pyridine*.—To a solution of [$AuCl_3(NCC_6H_4CH_3$-*p*)] (0.722 g, 1.72 mmol) in CH_2Cl_2 (5 cm^3), a solution of pyridine (py) (0.148 g, 1.87 mmol) in CH_2Cl_2 (5 cm^3) was added. There was an immediate reaction with formation of a yellow suspension. The i.r. spectrum of the liquid phase showed the ν_{CN} band of the free nitrile only, at 2 290 cm^{-1}. The suspension was filtered and the solid

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates for $[AuCl_3(NCC_6H_4CH_3\text{-}p)]$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Au	0.250 02(5)	0.481 10(3)	0.406 51(2)
Cl(1)	0.2494(5)	0.6433(2)	0.3399(2)
Cl(2)	0.2493(4)	0.5529(2)	0.5592(2)
Cl(3)	0.2514(5)	0.4034(2)	0.2573(2)
N	0.253(1)	0.3360(6)	0.4624(5)
C(1)	0.251(1)	0.2503(7)	0.4919(6)
C(2)	0.252(2)	−0.1747(8)	0.6388(8)
C(11)	0.253(1)	0.1447(7)	0.5281(6)
C(12)	0.253(2)	0.1278(8)	0.6286(6)
C(13)	0.255(2)	0.0245(8)	0.6618(6)
C(14)	0.251(1)	−0.0619(7)	0.6005(6)
C(15)	0.251(1)	−0.0430(7)	0.4996(6)
C(16)	0.251(1)	0.0599(7)	0.4640(6)

phase dried *in vacuo*. It was identified analytically as $[AuCl_3(py)]$.

Reaction between $[AuCl_3(NCC_6H_4CH_3\text{-}p)]$ *and* CO.—A solution of $[AuCl_3(NCC_6H_4CH_3\text{-}p)]$ (0.200 g, 0.48 mmol) in CH_2Cl_2 (5 cm^3) was saturated with CO at atmospheric pressure. After some days the i.r. spectrum of the solution showed the presence of the carbonyl band due to [AuCl(CO)][1] at 2 160 cm^{-1}.

Preparation of Complexes $AuCl_2(NCR)$ ($R = C_6H_4CH_3\text{-}p$ *or* $CH_2C_6H_5$).—Anhydrous gold(III) chloride (1.654 g, 5.45 mmol) was added to a solution of *p*-toluonitrile (8 cm^3, 7.84 g, 66.96 mmol) in CH_2Cl_2 (5 cm^3). After stirring for 20 d at room temperature, CCl_4 (40 cm^3) was added to the yellow suspension, the mixture filtered, and the solid product dried *in vacuo* (85% yield) (Found: C, 24.8; H, 1.5; Cl, 18.4; N, 3.3. Calc. for $C_8H_7AuCl_2N$: C, 25.0; H, 1.6; Cl, 18.5; N, 3.6%). Analogous results were obtained using phenylacetonitrile.

Crystal-structure Determination of $[AuCl_3(NCC_6H_4CH_3\text{-}p)]$.—*Crystal data.* $C_8H_7AuCl_3N$, $M = 420.48$, monclinic, $a = 6.669(2)$, $b = 12.574(3)$, $c = 13.740(3)$ Å, $\beta = 90.30(2)°$, $U = 1\,152.1(3)$ Å^3 (by least-squares refinement of the diffraction geometry of 25 reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $Z = 4$, $D_c = 2.424$ g cm^{-3}. Yellow needles, specimen size: 0.60 × 0.15 × 0.05 mm, $\mu(\text{Mo-}K_\alpha) = 134$ cm^{-1}, $F(000) = 768$. For all measurements the temperature was 190 K to avoid decomposition of the compound in the *X*-ray beam.

Data collection and processing. CAD4 diffractometer, 2θ–θ scan, graphite-monochromated Mo-K_α radiation; 1 954 reflections measured ($3 \leqslant \theta \leqslant 22°$), 1 509 unique [merging $R = 0.010$ after empirical absorption correction (azimuthal scans); max., min. transmission factors 0.89, 0.78], giving 1 246 reflections with $I > 3\sigma(I)$. Standard reflections with no significant deviation.

Structure analysis and refinement. Au position from inspection of Patterson map. Subsequent difference-Fourier synthesis revealed the positions of the Cl, N, C, and all H atoms. Full-matrix least-squares refinement (on *F*) with anisotropic thermal parameters for all non-H atoms, hydrogen positions of the methyl group with fixed thermal parameters, other H atoms were used in structure factor calculations only. 131 Refined parameters, final *R* and *R′* values 0.021, 0.025. Calculations were performed with the VAXSDP program system[13] on a VAX 11/750 computer. Atomic co-ordinates are listed in Table 1.

Results and Discussion

Although the chloride-bridged dimeric gold(III) chloride, Au_2Cl_6, reacts with benzene to give metallated products,[10] in the case of arenes containing basic functional groups, *i.e.* aromatic nitriles,[12,10d] azobenzene,[2,3] or 4,4′-azotoluene,[2,3] there is no metallation but chloride bridge cleavage with formation of derivatives $[AuCl_3L]$ where the organic group L is nitrogen-bonded to the metal.

Table 2. Nitrile stretching frequencies for $[AuCl_3(NCR)]$ and $AuCl_2(NCC_6H_4CH_3\text{-}p)$

		ν_{CN}/cm^{-1}	
Species	Solvent	Complex	Free ligand
$[AuCl_3(NCC_6H_5)]$	CH_2Cl_2	2 297	2 229
$[AuCl_3(NCC_6H_4CH_3\text{-}p)]$	CH_2Cl_2	2 291	2 228
	$C_2H_2Cl_4$	2 291	2 228
	Nujol	2 295	—
$[AuCl_3(NCCH_2C_6H_5)]$	CH_2Cl_2	2 329	2 252
$[AuCl_3(NCCH_3)]$	CH_3CN	2 347	2 250
$AuCl_2(NCC_6H_4CH_3\text{-}p)$	$C_2H_2Cl_4$	2 288	2 228
	Nujol	2 300	—

As far as nitriles are concerned, analogous results were obtained when the reaction was carried out at room temperature under anhydrous conditions using either the stoicheiometric amount or a large excess of the nitrile [see reaction (5); $R = C_6H_4CH_3\text{-}p$, $CH_2C_6H_5$, or C_6H_5].

$$Au_2Cl_6 + 2NCR \longrightarrow 2[AuCl_3(NCR)] \qquad (5)$$

It would be very interesting to define the conditions for metallation. At the moment we can confirm that anhydrous gold(III) chloride reacts very quickly with benzene, toluene, and chlorobenzene, but, if prior formation of an adduct $[AuCl_3L]$ is possible, the metallation reaction becomes very slow, if any.

The nitrile derivatives exhibit typical i.r. bands. The NC stretching vibrations of the complexes $[AuCl_3(NCR)]$ are reported in Table 2, together with the corresponding values for the free nitriles. There is an increase in frequency on going from the free ligand to the complex; this is the normal trend for nitrile complexes of main-group elements or transition-metal halides where no or very little back-donation[14–16] from the metal to the ligand operates. This behaviour is usual for gold in both oxidation states I and III in its co-ordination to carbon monoxide,[17] isocyanides,[18] or olefins.[19] Further information about the nature of the simple nitrile complexes came from the ^1H n.m.r. spectra (see Table 3). For $[AuCl_3(NCC_6H_4CH_3\text{-}p)]$ the ^1H n.m.r. spectrum in CH_2Cl_2 exhibits an AB quartet centred at τ 2.33 (four protons) and a singlet at τ 7.47 (three protons); $[AuCl_3(NCCH_2C_6H_5)]$ exhibits a multiplet at τ 2.53 and a singlet at τ 5.65. A molecular-weight determination of the *p*-toluonitrile derivative by cryoscopy in nitrobenzene indicated that the compound is monomeric in solution.

The weakly bonded *p*-toluonitrile ligand[20] was quickly displaced by pyridine according to reaction (6). The 4,4′-azotoluene derivative behaves analogously.[2] A further comparison between the two complexes showed that the nitrile derivative reacted with CO at room temperature and atmospheric pressure to give [AuCl(CO)] and free nitrile, whereas the 4,4′-azotoluene complex failed to react even at high pressure {at 150 atm only traces of [AuCl(CO)] were observed}. This difference is probably related to the higher lability of the nitrile ligand and in fact nitriles are often used in preparative co-ordination chemistry for their lability.[20]

$$[AuCl_3(NCC_6H_4CH_3\text{-}p)] + py \longrightarrow [AuCl_3(py)] + NCC_6H_4CH_3\text{-}p \qquad (6)$$

Since discrepancies existed between the results reported here

Table 3. Proton n.m.r. chemical shifts for $[AuCl_3(NCR)]$ ($R = C_6H_4CH_3$-*p* or $CH_2C_6H_5$) and $AuCl_2(NCC_6H_4CH_3$-*p*) compared with chemical shifts for the free ligands

		τ (from $SiMe_4$)	
Species	Solvent	Aromatic hydrogens	Aliphatic hydrogens^a
$NCC_6H_4CH_3$-*p*	CH_2Cl_2	2.63^b	7.62
	CD_3CN	2.66^b	7.63
$[AuCl_3(NCC_6H_4CH_3$-*p*)]	CH_2Cl_2	2.33^b	7.47
	CD_3CN	2.66^b	7.63
	$C_2H_2Cl_4$	2.44^b	7.49
$NCCH_2C_6H_5$	CD_3CN	2.67^c	6.20
$[AuCl_3(NCCH_2C_6H_5)]$	CH_2Cl_2	2.53^c	5.65
	CD_3CN	2.67^c	6.20
$AuCl_2(NCC_6H_4CH_3$-*p*)	CD_3CN	2.66^b	7.63
	$C_2H_2Cl_4$	2.44^b	7.49

^{a} Singlets. ^{b} AB quartet. ^{c} Multiplet.

Table 4. Bond lengths (Å) and angles (°) for $[AuCl_3(NCC_6H_4CH_3$-*p*)] with estimated standard deviations in parentheses

Au–Cl(1)	2.236(2)	Cl(1)–Au–Cl(2)	90.89(7)
Au–Cl(2)	2.284(2)	Cl(1)–Au–Cl(3)	91.30(8)
Au–Cl(3)	2.271(2)	Cl(2)–Au–Cl(3)	177.80(7)
Au–N	1.980(6)	Cl(1)–Au–N	178.6(2)
		Cl(2)–Au–N	90.4(2)
		Cl(3)–Au–N	87.4(2)
N–C(1)	1.151(7)	Au–N–C(1)	177.6(5)
C(1)–C(11)	1.418(9)	N–C(1)–C(11)	179.1(6)
C(2)–C(14)	1.512(9)	C(1)–C(11)–C(12)	119.2(6)
C(11)–C(12)	1.397(8)	C(1)–C(11)–C(16)	120.0(5)
C(12)–C(13)	1.377(9)	C(12)–C(11)–C(16)	120.8(6)
C(13)–C(14)	1.375(9)	C(11)–C(12)–C(13)	118.1(6)
C(14)–C(15)	1.406(8)	C(12)–C(13)–C(14)	122.8(6)
C(15)–C(16)	1.384(8)	C(13)–C(14)–C(15)	118.1(6)
C(16)–C(11)	1.382(8)	C(14)–C(15)–C(16)	120.4(6)
		C(11)–C(16)–C(15)	119.7(5)

Table 5. Bond lengths (Å) and angles (°) for Cu^I and Ag^I nitrile complexes compared with analogous data for $[AuCl_3(NCC_6H_4CH_3$-*p*)]

Complex	M–N–C	M–N	N–C	Ref.
$[Ag(ClO_4)\{NC(CH_2)_4CN\}_2]$*	162.7(17)	2.28(3)	1.11(4)	24*c*
$[CuCl(NCCH_3)]$	172.8	2.00(2)	1.14(1)	24*a*
$[CuCl(NCC_6H_5)]$	175.5(6)	1.949(7)	1.087(12)	24*b*
$[AuCl_3(NCC_6H_4CH_3$-*p*)]	177.6(5)	1.980(6)	1.151(7)	This work

* Polymeric compound.

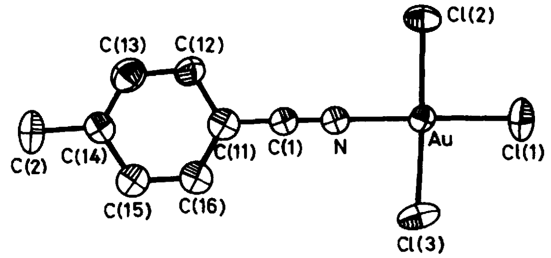

Figure 1. Molecular structure of $[AuCl_3(NCC_6H_4CH_3$-*p*)]

and some others,[10b] we decided to undertake an *X*-ray diffraction study of the *p*-toluonitrile complex in order fully to characterize one of the compounds and to increase the still limited range of structural data on gold(III) complexes.[21] The study confirmed that the product is a gold(III) end-on nitrile adduct with gold in its usual square co-ordination (Figure). The Au–N bond length [1.980(6) Å] (see Table 4) can be compared with the values of 2.01(2) Å in $[AuCl_3(NH_3)]$,[22] 2.08 Å (av.) in $[AuCl_3\{N_2(C_6H_4CH_3$-*p*$)_2\}]$,[2] 1.993(7) Å in $[AuCl_3(py)]$,[23] and 1.97 Å (av.) in $[AuCl_2(py)_2]Cl$.[23] It is interesting to note that the Cl atom *trans* to the nitrile has the shortest distance from Au. The angle Au–N–C(1) is 177.6(5)°, indicating no intramolecular interaction between the metal centre and aromatic ring. A comparison with the structural data of copper(I) and silver(I) complexes[24] is reported in Table 5. For the copper and silver complexes there are some deviations from linearity of the group M–N–C. Crystal packing effects[24a,b] or conformation requirements in the case of $NC(CH_2)_4CN$ bridging two silver ions[24c] are suggested to be responsible.

Until now analytical, spectroscopic, cryoscopic, and structural data confirm that the complexes obtained from anhydrous gold(III) chloride and nitriles containing aromatic groups are not metallated, and products having a Cl:Au ratio of 3:1 are accordingly observed. Nevertheless, when a large excess of the nitrile was used and the reaction mixture was stirred for some time (*ca.* 20 d) at room temperature (or for a shorter time at 50 °C), products were obtained with a Cl:Au ratio of 2:1 and containing one mole of nitrile per mole of gold (nitrile = *p*-toluonitrile or phenylacetonitrile). The i.r. spectra are almost superimposable with the spectra of analogous $[AuCl_3(NCR)]$ complexes except in the 400—200 cm^{-1} region, typical of the Au–Cl stretching absorptions. Specifically, the 2 000—1 600 cm^{-1} region, which is sensitive to aromatic ring substitution, is unaffected by the analytical composition of the product. In the 400—200 cm^{-1} region, $[AuCl_3(NCC_6H_4CH_3$-*p*)] has bands at 370(sh), 350s, and 280w br cm^{-1}, while $AuCl_2(NCC_6H_4CH_3$-*p*) has bands at 345s br, 280mw, and 260w cm^{-1}. The ^1H n.m.r. spectra in CD_3CN of $[AuCl_3(NCC_6H_4CH_3$-*p*)] and $AuCl_2(NCC_6H_4CH_3$-*p*) had the same pattern as free *p*-toluonitrile: an AB quartet centred at τ 2.66 and a singlet at τ 7.63 (see Table 3), probably due to the ring and methyl protons, respectively, as a consequence of the displacement reaction (7)

$$AuCl_n(NCC_6H_4CH_3\text{-}p) + CD_3CN \longrightarrow AuCl_n(NCCD_3) + NCC_6H_4CH_3\text{-}p \quad (7)$$

(n = 2 or 3). The ^1H n.m.r. spectrum in $C_2H_2Cl_4$, in which both products are very soluble, showed an AB quartet centred at τ 2.44 and a singlet at τ 7.49 due to co-ordinated *p*-toluonitrile. Moreover, reaction with pyridine gives free nitrile. On the basis of these results, we suggest that the product with n = 2 in equation (7) is an ionic mixed-valence product formed according to equation (8) ($R = C_6H_4CH_3$-*p* or $CH_2C_6H_5$).

$$Au_2Cl_6 + NCR \longrightarrow [AuCl_2(NCR)_2][AuCl_2] + \text{oxidized products} \quad (8)$$

Unfortunately attempts to grow single crystals failed, and i.r. and n.m.r. data only are not sufficient to obtain definitive indications about the structure. I.r. bands are observed at 350 cm^{-1} for $[Au(py)_2][AuCl_2]$,[25] 365 cm^{-1} for $[AuCl_2(py)_2]Cl\cdot H_2O$,[23] 371(sh), 362s, and 334(sh) cm^{-1} for $[AuCl_3(py)]$,[23] and 372s and 344s cm^{-1} for $[AuCl_2(py)_2][AuCl_2]$.[23] The i.r. spectrum of $AuCl_2(NCC_6H_4CH_3$-*p*) in the 400—200 cm^{-1} region is very simple compared with the previous complexes. The presence of a single, although broad, band at 345 cm^{-1} for the species $[AuCl_2(NCR)_2][AuCl_2]$ ($R = C_6H_4CH_3$-*p* or $CH_2C_6H_5$), for which at least two bands are expected, can be explained by the overlap of two almost coincident bands, due to $[AuCl_2]^-$ and $[AuCl_2(NCR)_2]^+$ ions. If the assignment is correct the ionic product of reaction (8) is probably the *trans* geometrical isomer, in view of the unique CN stretching of the co-ordinated nitrile at $\sim 2\,290$ cm^{-1}. Further studies are in progress to define the nature of the complexes and to characterize the oxidation products.

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References

1 D. Belli Dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 1973, **103**, 1099.

2 D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, and S. Merlino, *Gazz. Chim. Ital.*, 1978, **108**, 627.

3 R. Huttel and A. Konietzny, *Chem. Ber.*, 1973, **106**, 2098.

4 R. A. Potts, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1749.

5 (*a*) D. Belli Dell'Amico, F. Calderazzo, and F. Marchetti, *J. Chem. Soc., Dalton Trans.*, 1976, 1829; D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, S. Merlino, and G. Perego, *J. Chem. Soc., Chem. Commun.*, 1977, 31.

6 R. Roulet, N. Quang Lan, W. R. Mason, and G. P. Fenske, *Helv. Chim. Acta*, 1973, **56**, 2405.

7 R. Hüttel, H. Reinheimer, and K. Nowak, *Chem. Ber.*, 1968, **101**, 3761.

8 A. Sacco and M. Freni, *Gazz. Chim. Ital.*, 1956, **86**, 195.

9 D. De Filippo, F. Devillanova, and C. Preti, *Inorg. Chim. Acta*, 1971, **5**, 103.

10 (*a*) M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc.*, 1931, **53**, 3053; (*b*) M. S. Kharasch and T. M. Beck, *ibid.*, 1934, **56**, 2057; (*c*) K. S. Liddle and C. Parkin, *J. Chem. Soc., Chem. Commun.*, 1972, 26; (*d*) P. W. J. De Graaf, J. Boersma, and G. J. L. Van Der Kerk, *J. Organomet. Chem.*, 1976, **105**, 399.

11 P. K. Monaghan and R. J. Puddephatt, *Inorg. Chim. Acta*, 1975, **15**, 231.

12 F. Calderazzo and D. Belli Dell'Amico, *J. Organomet. Chem.*, 1974, **76**, C59.

13 B. A. Frenz, VAXSDP System, Version 2.2 of March 1985, B. A. Frenz, Texas, U.S.A. and Enraf–Nonius, Delft, The Netherlands.

14 R. A. Walton, *Q. Rev. Chem. Soc.*, 1965, **19**, 126 and refs. therein.

15 G. Beech, G. Marr, and S. J. Ashcroft, *J. Chem. Soc. A*, 1970, 2903.

16 B. N. Storhoff and H. C. Lewis, jun., *Coord. Chem. Rev.*, 1977, **23**, 1.

17 D. Belli Dell'Amico, F. Calderazzo, and G. Dell'Amico, *Gazz. Chim. Ital.*, 1977, **107**, 101.

18 (*a*) L. G. Vaughan and W. A. Sheppard, *J. Am. Chem. Soc.*, 1969, **91**, 6151; (*b*) J. A. McCleverty and M. M. M. da Mota, *J. Chem. Soc., Dalton Trans.*, 1973, 2571; (*c*) F. Bonati and G. Minghetti, *Gazz. Chim. Ital.*, 1973, **103**, 373.

19 (*a*) M. Herberhold, 'Metal π-Complexes,' Elsevier, Amsterdam, 1974, vol. 2, Part 2, pp. 32—50; (*b*) T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1559.

20 J. A. Davies and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79.

21 P. G. Jones, *Gold Bull.*, 1981, **14**, 159.

22 J. Strähle, J. Gelinek, and M. Kolmel, *Z. Anorg. Allg. Chem.*, 1979, **456**, 241.

23 H. N. Adams and J. Strähle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 65.

24 (*a*) M. Massaux, M. J. Bernard, and M. T. Le Bihan, *Bull. Soc. Fr. Mineral. Crystallogr.*, 1969, **92**, 118; (*b*) M. Massaux and M. T. Le Bihan, *Acta Crystallogr., Sect. B*, 1976, **321**, 586; (*c*) D. M. Barnhart, C. N. Caughlan, and Mazhar-Ul-Haque, *Inorg. Chem.*, 1969, **8**, 2768.

25 H. N. Adams, W. Hiller, and J. Strähle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 81.

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