SYNTHESIS AND X-RAY STRUCTURE OF PENTACARBONYL(7-η^1-CYCLOHEPTA-1,3,5-TRIENYL)RHENIUM(I)

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Summary

Synthesis by two routes of $(7\text{-}\eta^1\text{-}C_7H_7)Re(CO)_5$ (2), the first *monohapto*-cycloheptatrienyl derivative of a transition metal, is described. The first involves ultraviolet irradiation of the acyl $C_7H_7(CO)Re(CO)_5$ (1) in acetone at —78°C.

The second and preferred route involves reaction of $NaRe(CO)_5$ with $[C_7H_7]$-$[BF_4]$ in THF to form orange crystalline 2 in 90% yield. Activation enthalpy for thermal decomposition of 2 to form ditropyl and $Re_2(CO)_{10}$ is 30.4 ± 0.3 kcal mole^{-1}, a value close to the estimated strength of the C_7H_7—$Re(CO)_5$ bond. A single crystal X-ray diffraction study of 2 shows a nearly octahedral $Re(CO)_5$ group bonded in the quasi-axial position to the methylene carbon atom of the seven-membered ring, which has a boat conformation. NMR spectra are consistent with a similar structure as the exclusive or dominant form in solution.

Introduction

The analogy of tropylium cation, $C_7H_7^+$, to $C_5H_5^-$ and C_6H_6 was noted in the context of organotransition metal chemistry in 1956 [1]. Entry to the field by reaction of metal carbonyl anions such as $Na[Mn(CO)_5]$ [2] or $Na[(\eta\text{-}C_5H_5)Cr(CO)_3)]$ [3] with tropylium bromide appeared to be ruled out when these reactions led only to ditropyl and the metal carbonyl dimer. It was considered that the failure to obtain C_7H_7 complexes in this way was related to the strong oxidizing power of $C_7H_7^+$ and the strong reducing power of metal carbonyl hydrides and their derivatives [3], and it was eventually suggested [4] in the $Mn(CO)_5^-$ case that the σ (or η^1) intermediate was very unstable. The notion that *monohapto*-cycloheptatrienyl derivatives of transition metals were generally unstable appeared to receive support when a compound reported initially as $(\eta^5\text{-}C_5H_5)Fe(CO)_2(7\text{-}\eta^1\text{-}C_7H_7)$ [5] was reformulated [6] as $(\eta^5\text{-}C_5H_5)Fe(CO)$-$(\eta^3\text{-}C_7H_7)$.

Nevertheless, a cycloheptatrienyl derivative of tin was known [7,8] and its fluxional behavior was of considerable interest [7,9]. We therefore set out to reexamine the question of the stability of *monohapto*-cycloheptatrienyl derivatives of transition metals, taking as our starting point the report [10] that the bond dissociation energy $D[CH_3—M(CO)_5]$ was 22—25 kcal mole^{-1} greater for M = Re than for M = Mn. A preliminary report on the results has appeared [11], and we present here full details of the synthesis as well as the crystal and molecular structure of $(7\text{-}\eta^1\text{-}C_7H_7)Re(CO)_5$ (**2**).

Structural results on 2

The overall structure and numbering scheme is shown in Fig. 1. Table 1 gives atom coordinates, Table 2 gives bond distances, and Table 3 gives bond angles.

The cycloheptatrienyl ring is in a boat conformation, with alternating long and short carbon—carbon distances corresponding to the expected pattern of single and double bonds. The approximately octahedral pentacarbonylrhenium group is in the quasi-axial position, and the Re—C(7) bond length is 2.348(11) Å.

Atoms C(1), C(2), C(6), C(5) are coplanar to within 0.001 Å, and the dihedral angles of this reference plane with planes formed by C(2), C(3), C(4), C(5) and by C(1), C(6), C(7) are 26.6 and 39.0°, respectively.

Distortions of the equatorial carbonyl groups are such that those lying above the cycloheptatrienyl ring bend away from the ring, putting angles C(9)—Re—C(7) and C(8)—Re—C(7) in the 91—92° range; the other equatorial carbonyls bend away from the axial carbonyl so that angles C(11)—Re—C(7) and C(12)—
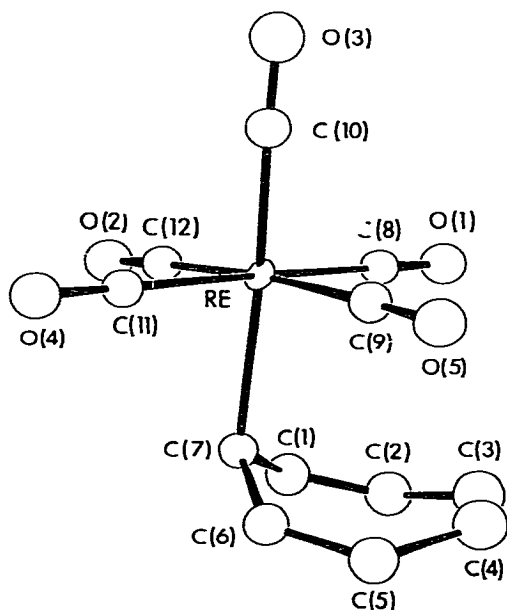

Fig. 1. The molecular structure of $(7\text{-}\eta^1\text{-}C_7H_7)Re(CO)_5$ (**2**). Thermal ellipsoids are drawn at the 50% level.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS [a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.20668(7)	0.09601(2)	0.28865(5)	0.02284(9)	0.00173(1)	0.01210(5)	0.00020(7)	0.0138(1)	0.00032(5)

Atom	x	y	z	$B(\text{Å})$	Atom	x	y	z	$B(\text{Å})$
O(1)	0.538(1)	0.0411(5)	0.167(1)	6.6(2)	C(9)	−0.017(2)	0.0710(6)	0.094(1)	4.3(2)
O(2)	0.549(2)	0.1482(5)	0.583(1)	7.4(3)	C(7)	0.227(2)	0.1908(6)	0.177(1)	4.3(3)
O(3)	0.189(2)	−0.0261(5)	0.452(1)	7.8(3)	C(6)	0.042(2)	0.2070(6)	0.046(1)	5.1(3)
O(4)	−0.125(1)	0.1532(4)	0.406(1)	5.5(2)	C(5)	−0.009(2)	0.1897(7)	−0.103(2)	6.0(3)
O(5)	−0.147(1)	0.0584(4)	−0.018(1)	5.8(2)	C(4)	0.109(3)	0.1494(8)	−0.169(2)	7.5(4)
C(8)	0.419(2)	0.0613(6)	0.213(1)	4.4(2)	C(3)	0.318(2)	0.1454(8)	−0.114(2)	7.7(4)
C(12)	0.424(2)	0.1274(6)	0.475(1)	4.7(3)	C(2)	0.459(2)	0.1806(8)	0.014(2)	6.8(4)
C(10)	0.197(2)	0.0207(7)	0.393(2)	5.4(3)	C(1)	0.418(2)	0.2000(7)	0.143(2)	6.0(3)
C(11)	−0.001(2)	0.1327(5)	0.364(1)	4.0(2)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}{}^{\star}h^2 + \beta_{22}{}^{\star}h^2 + \beta_{33}{}^{\star}l^2 + \beta_{12}{}^{\star}hk + \beta_{13}{}^{\star}hl + \beta_{23}{}^{\star}kl)]$. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

TABLE 2

BOND LENGTHS (Å) [a]

Re—C(8)	1.980(12)	O(4)—C(11)	1.143(12)
Re—C(12)	1.959(12)	O(5)—C(9)	1.132(12)
Re—C(10)	1.919(13)	C(7)—C(6)	1.462(15)
Re—C(11)	1.966(11)	C(7)—C(1)	1.48(2)
Re—C(9)	1.981(11)	C(6)—C(5)	1.32(2)
Re—C(7)	2.348(11)	C(5)—C(4)	1.47(2)
O(1)—C(8)	1.129(12)	C(4)—C(3)	1.37(2)
O(2)—C(12)	1.156(13)	C(3)—C(2)	1.46(2)
O(3)—C(10)	1.171(14)	C(2)—C(1)	1.35(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 3

BOND ANGLES (°) [a]

| C(8)—Re—C(12)	88.8(5)	Re—C(8)—O(1)	179.(1)
C(8)—Re—C(10)	89.1(5)	Re—C(12)—O(2)	177.(1)
C(8)—Re—C(11)	178.4(4)	Re—C(10)—O(3)	178.(1)
C(8)—Re—C(9)	92.7(5)	Re—C(11)—O(4)	178.(1)
C(8)—Re—C(7)	92.3(4)	Re—C(9)—O(5)	178.(1)
C(12)—Re—C(10)	92.1(5)	Re—C(7)—C(6)	113.3(8)
C(12)—Re—C(11)	90.2(5)	Re—C(7)—C(1)	113.5(8)
C(12)—Re—C(9)	175.4(5)	C(6)—C(7)—C(1)	114.(1)
C(12)—Re—C(7)	84.6(4)	C(7)—C(6)—C(5)	127.(1)
C(10)—Re—C(11)	92.3(5)	C(6)—C(5)—C(4)	126.(1)
C(10)—Re—C(9)	92.2(5)	C(5)—C(4)—C(3)	124.(1)
C(10)—Re—C(7)	176.5(5)	C(4)—C(3)—C(2)	127.(2)
C(11)—Re—C(9)	88.2(4)	C(3)—C(2)—C(1)	124.(1)
C(11)—Re—C(7)	86.4(4)	C(7)—C(1)—C(2)	127.(1)
C(9)—Re—C(7)	91.0(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Re—C(7) are 86.4 and 84.6°. Nonbonding intramolecular contacts between C(8)—O(1) and C(9)—O(5) and the ring carbons range from 3.08 to 3.37 Å. There are no abnormally short intermolecular contacts, the shortest of these being O—O distances between 3.18 and 3.24 Å.

Discussion

The title compound **2** has been prepared as an orange crystalline solid melting without noticeable decomposition at 74°C. The formulation of the compound from analytical and spectroscopic results has been fully substantiated by X-ray diffraction study. Color is not unprecedented in alkyl pentacarbonyl-rhenium derivatives, since the benzyl complex is reported to be bright yellow, although the methyl and phenyl compounds are colorless [12].

Two routes for preparation of the compound are shown in Scheme 1. The direct route, involving pentacarbonylrhenate(—I) anion and tropylium cation,
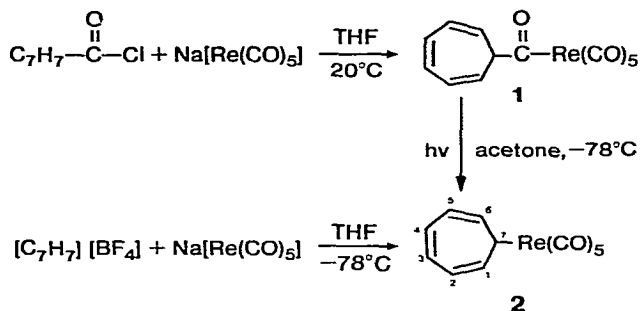
SCHEME 1. Synthesis of Compounds 1 and 2.

affords **2** in 90% yield from readily available starting materials and is the method of choice. The route via the acyl **1** is nevertheless of interest and was the approach we first took on the assumption that the tropylium cation-carbonyl anion reaction was doomed to failure. Only after the stability of **2** was clear did we investigate the alternative route.

The interesting work of Whitesides and Budnik on analogous reactions of the $Mn(CO)_5^-$ anion is pertinent [13]. These authors confirmed the earlier results of Abel et al. [2] by showing that the reaction of $Mn(CO)_5^-$ with $[C_7H_7][BF_4]$, even at $-78°C$, formed only the respective dimers. They further found that irradiation of $C_7H_7(CO)Mn(CO)_5$ afforded not $(7\text{-}\eta^1\text{-}C_7H_7)Mn(CO)_5$ but $(\eta^5\text{-}C_7H_7)Mn(CO)_3$.

The great contrast between manganese and rhenium is fully explicable in terms of the strengths of Mn—C and Re—C bonds. One must also note the extensive stabilization of the tropyl (or tropenyl) radical $C_7H_7{}^\bullet$; $D[C_7H_7\text{—}C_7H_7]$ is 35 kcal mole^{-1} [14] while $D[CH_3\text{—}CH_3]$ is 88 kcal mole^{-1} [15], so that the stabilization of a $C_7H_7{}^\bullet$ radical relative to $CH_3{}^\bullet$ is about 26 kcal mole^{-1}. Values for $D[CH_3\text{—}Mn(CO)_5]$ are 27.9 ± 2.3 or 30.9 ± 2.3 kcal mole^{-1} [10], which would place $D[C_7H_7\text{—}Mn(CO)_5]$ in the range of 2—5 kcal mole^{-1}. Its instability even at $-78°C$ is not surprising!

For rhenium $D[CH_3\text{—}Re(CO)_5] = 53.2 \pm 2.5$ kcal mole^{-1} [10], so $D[C_7H_7\text{—}Re(CO)_5]$ should be in the vicinity of 27 kcal mole^{-1}. We have studied the first order decomposition of **2** in dioxane-d_8 between 54.3 and 83.4°C (eq. 1) and find $\Delta H^{\neq}$ 30.4 ± 0.3 kcal mole^{-1}. The reasonable agreement between estimated

$$(7\text{-}\eta^1\text{-}C_7H_7)Re(CO)_5 \xrightarrow[\text{dioxane}]{\Delta} 1/2(C_7H_7)_2 + 1/2Re_2(CO)_{10} \tag{1}$$
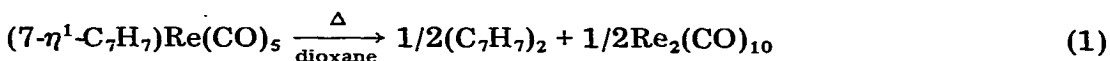
bond dissociation energy and measured activation energy for thermal decomposition is gratifying. Owing to radical recombination, the true rate of rhenium-carbon homolysis could be greater than the rate of decomposition; the value of 30.4 kcal mole^{-1} would represent an upper limit to the bond dissociation energy.

Structure of 2 in the solid state and in solution

In the crystalline state (structures **2a** and **2b**) the pentacarbonylrhenium group occupies the quasi-axial position (**2a**) with dihedral angles as shown. In

this respect it resembles the structure determined for $(7\text{-}\eta^1\text{-}C_7H_7)Sn(C_6H_5)_3$ [8].

2a
(Quasi-axial)

2b
(Quasi-equatorial)
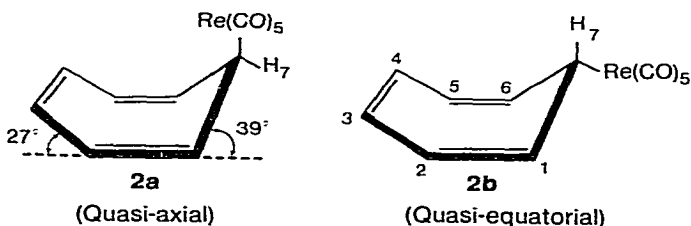
The geometry of the seven-membered ring is quite similar in the two compounds, as shown by the dihedral angles indicated in 2a: these are 27 and 39° in the rhenium derivative and we calculate the corresponding angles in the tin compound as 29 and 46°, respectively.

The length of the Re—C(7) bond is 2.348(11) Å. This value is the same within error as the Re—CH₃ bond in $(\eta^5\text{-}C_5H_5)Re(CO)_2Br(CH_3)$, 2.32(4) Å [16], and significantly longer than the mean Re—CH₃ distance of 2.24 Å in $(\eta^5\text{-}C_5H_5)$-$(\eta^4\text{-}C_5H_5CH_3)Re(CH_3)_2$ [17]. It is unfortunate that a more suitable structure for comparison purposes is not available, but to our knowledge no X-ray structure has been reported for a compound in which the Re(CO)₅ group is bonded to an sp^3 carbon atom. Since the C(7)—Re(CO)₅ bond in 2 is only about half as strong as a "normal" $C(sp^3)$—Re(CO)₅ bond (vide supra), a comparison of otherwise closely matched compounds would be of interest.

The question of the conformation of 2 in solution, that is whether 2a, 2b, or a mixture of both, is significant in view of the observed 1,2 shift of the metal that occurs [11]. Thus, if 2b were the solution conformation, it could be argued that a migration of Re(CO)₅ from C(7) to C(3) or C(4) was blocked by an unfavorable spatial relationship.

Before the solid state structure was determined, we had inferred from NMR evidence that 2a was the dominant or exclusive form in solution [11]. The vicinal coupling constant $^3J(H(1)\text{—}H(7))$ is 8.5 Hz, similar to the 8 Hz value in $(7\text{-}\eta^1\text{-}C_7H_7)Sn(C_6H_5)_3$ [9]; values of $^3J(H(1)\text{—}H(7))$ are expected to be smaller for H(7) in the axial position on the basis of the Karplus relation. This has been borne out by vicinal couplings observed in low temperature static spectra of both conformers of the 7-CHO derivative [18]; $^3J(H(1)\text{—}H(7))$ was 9.2 Hz for equatorial H(7) and <5Hz for axial H(7).

When the 100 MHz ¹H NMR spectrum of 2 was determined (in 4/1 CHF₂Cl/CD₂Cl₂) at a series of temperatures down to —150°C, the chemical shift of H(7) and the coupling constant $^3J(H(1)\text{—}H(7))$ remained unchanged; there was some line broadening (from ~0.5 to ~3—4 Hz) likely due to solvent viscosity, but no indication that the spectrum was resolving itself into two static forms. Barring coincidence, we tentatively conclude on the following grounds that 2a is the dominant or exclusive form in solution.

In cycloheptatriene itself [19,20] and in a number of its organic 7-monosubstituted derivatives [18,21,22] there is a chemical shift difference on the order of 1 ppm between axial and equatorial H(7); variation of the 2a ⇌ 2b equilibrium constant with temperature should therefore cause an observable change in the averaged chemical shift provided 2b is present in significant concentration. This has been observed for several organic 7-monosubstituted compounds above

coalescence [23]. A similar argument would apply to the averaged coupling constant. Moreover, in the organic derivatives examined (7-R—C_7H_7: R = CHO [18], COOH [22], CN [21], H [19,20]) interconversion of conformations becomes slow on the NMR time scale in the —130 to —150°C range, and H(7) signals of both conformers are observed. Our conclusion would stand unless some combination of the following possibilities obtains: (1) the **2a** ⇌ **2b** equilibrium constant varies only slightly with temperature over a range of more than 150°C; (2) H(7) chemical shifts and coupling constants in **2a** and **2b** are nearly the same; (3) the activation energy for **2a**—**2b** interconversion is lower than in similar organic derivatives.

Experimental

General procedures, reagents, and instrumentation

Reactions were carried out in an atmosphere of dry nitrogen using solvents dried by standard procedures and distilled immediately before use. Deca-carbonyldirhenium was purchased from Strem Chemicals, Inc.; tropylium tetrafluoroborate and cyclopentatriene were obtained from Aldrich. The preparation of 7-cycloheptatrienylacyl chloride followed the literature method [24]; an improved preparation of the carboxylic acid precursor has been reported [25].

Infrared spectra were recorded on a Nicolet MX-1 FT instrument and a Bruker WH-400 spectrometer was used to obtain ^{1}H and ^{13}C NMR spectra; NMR spectra of **2** to —150°C were measured on a Varian HA-100/Digilab FT system.

Pentacarbonyl(7-cycloheptatrienylacyl)rhenium (1)

A solution of C_7H_7(CO)Cl (2.04 g, 13.2 mmol) in 15 ml tetrahydrofuran (THF) was added at room temperature over 30 min to a solution of NaRe(CO)$_5$ prepared from 4.32 g (6.6 mmol) Re$_2$(CO)$_{10}$ by reaction with Na/Hg in 100 ml THF. After stirring for 30 min the volume of THF was reduced under vacuum to 20 ml; the solution was diluted with water (200 ml) and extracted with 5 30-ml portions of hexane. The extracts were dried, filtered, and cooled to —10°C. Later cooling to —78°C completed the crystallization, affording **1** as pale yellow crystals m.p. 98°C (4.1 g, 70%).

IR (cyclohexane, cm^{-1}, ν(CO) with intensity and assignment in C_{4v} symmetry): 2132 (w,A$_1$), 2061(w,B$_1$), 2023(s,E), 2014(s,E), 1999(s,A$_1$), 1637,1626(w, acyl CO). ^{1}H NMR (methylcyclohexane-d_{14}, δ, assignments by decoupling): 6.51 (m,H(3,4)), 6.18 (m,H(2,5)), 5.12 (m,H(1,6)), 2.50 (t, H(7), $^3J_{17}$ 5.8 Hz).

Analysis. Found: C, 35.08; H, 1.70. $C_{13}H_7O_6$Re calcd: C, 35.04; H, 1.57%.

Pentacarbonyl (7-η^1-cycloheptatrienyl)rhenium (2)

Method A A sample of **1** (890 mg, 2 mmol) in 40 ml dry, oxygen-free acetone was placed in a quartz flask which was partly immersed in a Dry Ice acetone bath and irradiated for 12 h using a Hanovia 140 W lamp. Acetone was removed in vacuum and the orange residue extracted with 4 15-ml portions of hexane. Cooling the extracts to —78°C gave **2** contaminated with a little **1**. Two recrystallizations from hexane afforded pure **2** as orange needles m.p. 74°C (500 mg, 60%).

IR (cyclohexane, cm^{-1}, ν(CO) with intensity and assignment in C_{4v} symmetry): 2120 (w, A$_1$), 2015 (s,E), 1983 (m,A$_1$). ^{1}H NMR (20°C, dioxane-d_8,δ) 5.92 (m,H(3,4)), 5.44 (m, H(1,6)), 5.16 (m,H(2,5)), 3.16(tt,H(7),$^3J_{17}$ 8.5, $^4J_{27}$ 1.0 Hz). ^{13}C NMR (0°C, THF-d_8,δ) 18.1(C(7)), 122.1(C(2,5)), 136.1(C(3,4)) 141.3(C(1,6)); 182.0(1C, axial CO), 187.3 (4C, equatorial CO). UV-VIS (dioxane, λ_{max}nm,ϵ): 278(5200), 394(2500). Analysis. Found: C, 34.54; H, 1.78. C$_{12}$H$_7$O$_5$Re calcd.: C, 34.52; H, 1.69%. Mass spectrum (16 eV, 35°C): molecular ion M^+ at 418 (correct isotope pattern); $(M - nCO)^+$, n = 2—5; $(M - C_7H_7^+$; C$_7$H$_7^+$) (base peak).

Method B NaRe(CO)$_5$ (10 mmol) in 100 ml THF was cooled to —78°C (a white precipitate formed) and solid C$_7$H$_7$BF$_4$ (1.78 g, 10 mmol) was added in one portion. The mixture was stirred at —78°C for 1 h, THF was removed in vacuum and the residue extracted with 3 20-ml portions of hexane. The combined extracts were filtered and cooled to —78°C affording 2 (3.8 g, 90%) identical to that of method A.

Thermal decomposition of 2

Samples of **2** (0.20 M) in dioxane-d_8 were freeze-thaw degassed in vacuum in NMR tubes which were then sealed off. ^{1}H NMR was used to monitor the first order disappearance of **2** at three temperatures: T, k: 54.3°C, 2.60 $\times$ 10^{-5} sec^{-1}; 68.4°C, 2.00 $\times$ 10^{-4} sec^{-1}; 83.4°C, 1.33 $\times$ 10^{-3} sec^{-1}. Calculated activation parameters (error limits correspond to one standard deviation): $\Delta H^{\neq}$ = 30.4 $\pm$ 0.3 kcal mol^{-1}; $\Delta S^{\neq}$ = 13 $\pm$ 1 e.u.; $\Delta G^{\neq}_{300}$ = 26.5 $\pm$ 0.5 kcal mol^{-1}. The major products of the thermal decomposition were (C$_7$H$_7$)$_2$ and Re$_2$(CO)$_{10}$ with small amounts (1—5%) of C$_7$H$_8$.

X-ray structure of 2.

The determination was performed by the crystallographic staff of Molecular Structure Corporation, College Station, Texas, U.S.A., using an Enraf—Nonius CAD4 diffractometer. A red prismatic crystal of dimensions ca. 0.12 $\times$ 0.12 $\times$ 0.10 mm was used for data collection. Hydrogen atoms were not included in the calculations. Only the 1487 reflections having $I > 3\sigma$ were included in the refinement. The final cycle included 78 variable parameters and converged with unweighted and weighted agreement factors of 0.038 and 0.049 respectively.

Crystal data: monoclinic, space group $P2_1/c$; a 6.962(2), b 22.099(3), c 8.955(1) Å; β 109.91(2)°; V 1295.4 Å^3; Z = 4; ρ(calc) 2.14 g cm^{-3}; μ 99.2 cm^{-1} for Mo-K_α radiation.

Acknowledgement

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