CYCLOPENTADIENYL SUBSTITUTED DIETHYLAMINOCARBYNE COMPLEXES OF TUNGSTEN IN A HIGHER OXIDATION STATE

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Abstract—The reaction of an equimolar mixture of $(\eta^{5}-C_{5}H_{5})(I)_{2}(CO)W\equivCNEt_{2}$ (1) and $t-C_{4}H_{9}NC$ in THF at 50°C, results in the replacement of the CO ligand by isocyanide and formation of $(\eta^{5}-C_{5}H_{5})(I)_{2}(t-C_{4}H_{9}NC)W\equivCNEt_{2}$ (2). Complex 2 reacts further with $t-C_{4}H_{9}NC$ in refluxing THF with displacement of the iodide ligand from the coordination sphere to give the cationic carbyne complex $[(\eta^{5}-C_{5}H_{5})(I)(t-C_{4}H_{9}NC)_{2}W\equivCNEt_{2}]^{+}I^{-}$ (3). A new route to 2 in three steps has also been developed. The starting material, *mer*-I($t-C_{4}H_{9}NC$)₃W \equiv CNEt₂ (4), is transformed with KC₃H₅ in refluxing THF to $(\eta^{5}-C_{5}H_{5})(I)(t-C_{4}H_{9}NC)(CO)W\equivCNEt_{2}$ (5). Complex 5 is then oxidized with elemental iodine in CH₂Cl₂ to give $[(\eta^{5}-C_{5}H_{5})(I)(t-C_{4}H_{9}NC)(CO)W\equivCNEt_{2}]^{+}I^{-}$ (6), the first cationic, carbonyl-containing carbyne complex of tungsten in a higher oxidation state. Finally, 6 is decarbonylated thermally in boiling THF to 2. The composition and structure of the new complexes 2, 3, 5 and 6 have been determined by total elemental analyses and IR, ¹H NMR, ¹³C NMR spectroscopies, as well as by mass spectrometry. The non-ionic nature of 2 and ionic nature of 6 in solution, have been confirmed by conductivity measurements.

Complexes containing a metal-carbon triple bond are divided into two classes. Class (a) includes compounds of low valent metals, which are known as Fischer type carbyne complexes. In these complexes, the electron-rich metal is stabilized by good π acceptor ligands such as CO, e.g. trans- $X(CO)_4M \equiv CR$ (X = halogen; M = Cr, Mo, W; $R = aryl or alkyl group).^{1}$ Class (b) contains complexes of high valent metals, i.e. Schrock type alkylidyne complexes. In these complexes, the electron-deficient metal is stabilized by good π donor ligands, such as halogen or alkoxy ligands, e.g. X_3 (dme) $W \equiv CCMe_3$ (X = halogen; dme = 1,2dimethoxyethane).²

Striking differences in the reactivity exist between class (a) and (b) compounds. This is most impressively demonstrated by their reactions with alkynes. Fischer type carbyne complexes catalyse alkyne polymerization, while Schrock type alkylidyne complexes function as alkyne metathesis catalysts.^{3,4}

In our development of the chemistry of substituted tungsten carbyne complexes with the general formula $I(CO)_2L_2W \equiv CNEt_2$ ($L = C_5H_5N$, PMe₃, *t*-C₄H₉NC, L₂ = 2,2'-bipy, *o*-phen), we have demonstrated that their oxidative decarbonylation with iodine gives (I)₃(CO)L₂W=CNEt₂ in high yield.⁵⁻⁸

These complexes are unique, because they combine features of both Fischer type carbyne complexes, such as π -acceptor CO ligands, and Schrock type alkylidyne complexes, i.e. a high valent metal centre. Therefore, new, interesting reactivity patterns are expected. We first studied their reactions with nucleophiles and found two reaction pathways to be predominant: (a) Substitution of the labile CO ligand and one iodide ligand by the nucleophile to form cationic carbyne complexes, e.g. the reaction of $(I)_3(CO)L_2W \equiv CNEt_2$ with $t-C_4H_9NC$ to give $[(I)_2(t-C_4H_9NC)_2L_2W \equiv CNEt_2]^+I^ (L_2 = 2, 2'$ bipy, *o*-phen; $L = t-C_4H_9NC$ ^{7,8} and (b) reductive elimination of iodine to give low valent, neutral or cationic carbyne complexes, e.g. the reaction of $(I)_3(CO)(PMe_3)_2W \equiv CNEt_2 \text{ or } (I)_3(CO)L_2W \equiv$ $CNEt_2$ (L₂ = 2,2'-bipy, *o*-phen) with PMe₃ to give $mer-I(PMe_3)_3(CO)W \equiv CNEt_2$ or $[(PMe_3)_2(CO)]$ $L_2W \equiv CNEt_2]^+I^-$ ($L_2 = 2,2'$ -bipy, *o*-phen).^{5,6} To

extend our studies on cyclopentadienyl (cp) substituted carbyne complexes, we have first developed a high yield route to $(\eta^{5}-C_{5}R_{5})(CO)_{2}W$ $(\mathbf{R}=\mathbf{H},$ $\equiv CNEt_2$ Me) and subsequently decarbonylated these complexes to give $(\eta^{5}-C_{5}R_{5})$ $(X)_2(CO)W \equiv CNEt_2 (R = H, Me; X = Br, I).^{9,10}$ We have found differences in the reactivity of $(\eta^{5}-C_{5}H_{5})(I)_{2}(CO)W \equiv CNEt_{2}$ compared to the corresponding $(I)_3(CO)L_2W \equiv CNEt_2$ complexes $(L_2 = 2,2'-bipy, o-phen; L = PMe_3, t-C_4H_9NC).$ Thus a reaction with PMe₃ occurs only at elevated temperatures; it leads to the displacement of the Cp ligand and reductive elimination of iodine to form low valent trimethylphosphinesubstituted carbyne complexes. The expected product, $(\eta^5 - C_5 H_5)(PMe_3)(CO)W \equiv CNEt_2$, was not observed.¹¹ This result has prompted us to investigate the reaction of $(\eta^5 - C_5 H_5)(I)_2(CO)W \equiv CNEt_2$ with $t-C_4H_9NC$.

RESULTS AND DISCUSSION

The reaction of 1 with $t-C_4H_9NC$ (molar ratio 1:1.2) in THF at 50°C, yields quantitatively the substitution product 2 [eq. (1)].

This product is isolated as a purple, microcrystalline solid, which is only slightly sensitive to air and moisture, soluble in CH_2Cl_2 , THF and toluene, but insoluble in Et_2O and *n*-pentane (m.p. 110°C).

Complex 2 reacts with $t-C_4H_9NC$ in boiling THF with the elimination of one iodide ligand from the coordination sphere and formation of the yellow, cationic carbyne complex 3 [eq. (2)]. This product is soluble in CH₂Cl₂, sparingly soluble in cold THF and toluene, but insoluble in Et₂O and *n*-pentane. Complex 3 undergoes decomposition in a sealed capillary at 135°C. A slow halogen exchange (iodide for chloride) occurred in a solution of 3 in CH₂Cl₂ at room temperature. This reaction is accelerated in boiling CH₂Cl₂ and leads to mixed halogen substitution products.¹¹

A different route to 2 has been developed requiring three steps. The first step involves the reaction of the easily available *mer*-I(t-C₄H₉NC)₃(CO)W \equiv CNEt₂ (4)¹² with KC₅H₅ in refluxing THF to give 5 [eq. (3)]. Complex 5 is an extremely air-sensitive, yellow oil, which is very soluble in CH₂Cl₂, THF, Et₂O and *n*-pentane. Complex 5 is then quantitatively transformed with elemental iodine to 6, the



first carbonyl containing, cationic carbyne complex of tungsten in a higher oxidation state [eq. (4)]:

the coordinated isonitrile and carbonyl ligands (Table 1).



This product is obtained as an orange, microcrystalline powder, which is very soluble in CH_2Cl_2 , sparingly soluble in cold THF and toluene, but insoluble in Et_2O and *n*-pentane. Decomposition of **6** is observed in a sealed capillary at 108°C.

In the last step, 6 is thermally decarbonylated to quantitatively give 2 [eq. (5)]:

A shift of the v(C = N+) absorptions to higher frequency is observed when the IR data of 2, 3 and 6 are compared. This shift can be attributed to a reduction of the electron density at the metal, and the simultaneous weakening of the metal isonitrile back-bonding. The same trend is observed for the



We assume a piano-stool geometry for complexes 2, 3 and 6, in agreement with MO-calculations on CpML₄ complexes, which favour energetically this structure over an alternative C_5H_5 -capped trigonal bipyramidal structure.¹³ The solution IR spectra of the new compounds, 2, 3, 5 and 6, show characteristic absorptions for the stretching vibrations of

v(C=0) band of compound 1 (v(C=0) in CH₂Cl₂, 2008 cm⁻¹)⁹ and 6 (v(C=0) in CH₂Cl₂, 2053 cm⁻¹), due to the weaker metal carbonyl backbonding in 6 compared with 2. In KBr, the complexes exhibit a strong band around 1600 cm⁻¹, which may be assigned to a v(C=N) vibration. This

	1604
—	
_	1615
0 s	
1 s —	
1829 s	
1845 s	
1860 s	
2053 s	1639
2041 s	
2041 s	
	1845 s 1860 s 2053 s 2041 s 2041 s

Table 1. v(C=N+), v(C=O) and v(C=N) stretching vibrations of 2, 3, 5 and 6 in cm⁻¹

"v(C=N) in KBr solvent.



Fig. 1. Resonance forms for the bonding in the carbyne ligand.

band displays the strong interaction of the metalcarbon triple bond with the lone pair of nitrogen (Fig. 1, resonance form \mathbf{B}).

The contribution of resonance form **B** to the bonding description of the carbyne ligand is diminished in **2** compared with **3** and **6**, due to an enhancement of the electron density at the metal centre. Therefore, a shift of the ν (C=N) vibration to lower frequency is observed. A similar trend has already been reported for other diethylaminocarbyne complexes of tungsten in both lower and higher oxidation states.^{5,6,8,14}

The triplets for the methyl protons of the diethylamino group observed in the ¹H NMR spectra of 2, 3, 5 and 6, confirm the free rotation of the ethyl groups around the carbyne–carbon– nitrogen bond (Table 2). A singlet is obtained for the *t*-butyl groups of the isonitrile ligands in 3, showing their *trans*-orientation. Complexes 5 and 6 are chiral, therefore, the protons of the methylene groups in the carbyne ligand are diastereotopic and give a signal of four overlapping quartets, which may be assigned in an ABX₃ spin system:



The same splitting is observed for the signals of the methylene protons in 2, which must, therefore, also be diastereotopic. These facts suggest a structure of low symmetry with a *cis*-orientation of the iodide ligands. In contrast, the t-C₄H₉NC ligands in 3 are *trans*-oriented and the molecule contains a plane of symmetry; the methylene protons are therefore homotopic and give rise to a quartet.

Resonances, expected for the carbyne carbons in cyclopentadienyl-substituted diethylaminocarbyne

Complex	NCH_2CH_3	t-C₄H ₉ NC	NCH ₂ CH ₃	C_5H_5	<i>T</i> (°C)
2	$\frac{1.33 (6, t)}{^{3}J_{\rm HH}} = 7.3$	1.53 (9, s)	$3.45 (2, dq)$ ${}^{2}J_{H_{A}H_{B}} = 13.1$ ${}^{3}J_{H_{A}H_{X}} = 7.3;$ $3.52 (2, dq)$ ${}^{2}J_{H_{A}H_{B}} = 13.1$ ${}^{3}J_{H_{B}H_{X}} = 7.3$	5.43 (5, s)	20
3	1.29 (6, t) ${}^{3}J_{\rm HH} = 7.3$	1.55 (18, s)	3.48 (4, q) ${}^{3}J_{\rm HH} = 7.3$	5.63 (5, s)	0
5	1.09 (6, t) ${}^{3}J_{\rm HH} = 7.3$	1.24 (9, s)	2.83 (2, dq) ${}^{2}J_{H_{A}H_{B}} = 13.2$ ${}^{3}J_{H_{A}H_{X}} = 7.3$; 2.91 (2, dq) ${}^{2}J_{H_{A}H_{B}} = 13.2$ ${}^{3}J_{H_{B}H_{X}} = 7.3$	5.32 (5, s)	20
6	1.32 (6, t) ${}^{3}J_{\rm HH} = 7.3$	1.60 (9, s)	$3.59 (2, dq)$ ${}^{2}J_{H_{A}H_{B}} = 13.2$ ${}^{3}J_{H_{A}H_{X}} = 7.3;$ $3.63 (2, dq)$ ${}^{2}J_{H_{A}H_{B}} = 13.2$ ${}^{3}J_{H_{B}H_{X}} = 7.3$	6.02 (5, s)	20

Table 2. ¹H NMR spectroscopic data of 2, 3 and 6 in CD₂Cl₂ and 5 in C₆D₆; chemical shifts in δ , relative to the solvent (CDHCl₂, $\delta = 5.32$ ppm; C₆D₆, $\delta = 7.15$ ppm); relative intensities and multiplicities in parentheses, coupling constants in Hz

Complex	NCH ₂ CH ₃	Me ₃ CNC	NCH ₂ CH ₃	Me ₃ CNC	C₅H₅	Me ₃ CNC	WCO	W≡C	<i>T</i> (°C)
2	14.7	30.9	48.9	59.3	94.7	150.3		305.5	20
3	14.5	30.1	49.1	59.9	93.3	136.2		302.3	0
5	14.4	31.6	45.6	58.7	89.7	202.8	226.7	259.9	20
6	14.3	30.1	50.1	61.0	94.9	127.8	201.5	302.3	20

Table 3. ¹³C NMR spectroscopic data of 2, 3 and 6 in CD₂Cl₂ and 5 in C₆D₆; chemical shifts in δ , relative to the solvent (CD₂Cl₂, $\delta = 53.8$ ppm; C₆D₆, $\delta = 128.0$ ppm)

complexes of tungsten, are observed in the ${}^{13}C$ - ${}^{1}H$ NMR spectra of 2, 3, 5 and 6 (Table 3).^{9,10}

The isonitrile carbons appear as broad singlets, because of the quadrupol relaxation of nitrogen. Therefore any ¹³C-¹⁴N coupling cannot be resolved. Comparing the data of 2, 3 and 6, an upfield shift of the isonitrile carbon resonance is observed. This can be explained by the weaker metal-isonitrile back-bonding (6 < 3 < 2) and is in agreement with results obtained earlier for other tungsten isonitrile complexes.^{8,12,14,15} For the same reason, the strong metal-isonitrile back-bonding in 5 causes an extremely large downfield shift of the isonitrile carbon signal. This is independently demonstrated by the shift of the $v(C \equiv N+)$ vibration in the IR spectrum of 5 to a considerably lower frequency ($v(C \equiv N+)$ in CH₂Cl₂, 1925 cm⁻¹) compared with that of the free ligand ($v(C \equiv N+)$) in CH_2Cl_2 , 2140 cm⁻¹).

The conductance of 6 in 1,2-dichloroethane is of the same magnitude ($c = 4.6 \times 10^{-4} \mod dm^{-3}$, t = 19.8°C, $\Lambda = 31 \ \Omega^{-1} \ cm^2 \ mol^{-1}$) as that of NR⁴₄X⁻ (R = "bu, "pr; X = Br, I, PF₆) and other ionic diethylaminocarbyne complexes of tungsten in low and high oxidation states.^{6-8,16} The conductivity increases with decreasing concentration of the complex, and proves independently the ionic nature of 6 in solution. In contrast, 1,2-dichloroethane solutions of 1 and 2 are not conducting.

The mass spectral data of 2, 3, 5 and 6 (Table 4) reveal characteristic fragmentation patterns of isonitrile-substituted diethylaminocarbyne complexes. Loss of I or t-C₄H₉NC, elimination of isobutylene (Me₂C=CH₂) from the t-C₄H₉NC ligand or C₂H₅ from the carbyne ligand are observed. Using the SIMS method for complex 3, the parent cation $[(\eta^{5}$ -C₅H₅)(I)(t-C₄H₉NC)₂W=CNEt₂]⁺ (K⁺: m/z = 626) is observed. Complex 6 decom-

m/z(relative ¹⁸⁴W Complex isotope) Tentative assignment 2 543 $[M-I]^+$ 487 $[M-I-Me_2C=CH_2]^+$ 626 K+ 3 [K--t-C₄H₉NC]⁺ 543 $[K-t-C_4H_9NC-Me_2C=CH_2]^+$ 487 $[K-t-C_4H_9NC-Me_2C=CH_2-C_2H_5]^+$ 458 M^+ 5 444 388 $[M-Me_2C=CH_2]^+$ $[M-Me_2C=CH_2-CO]^+$ 360 331 $[M - Me_2C = CH_2 - CO - C_2H_5]^+$ 6 670 [M---CO]+ $[M-CO-t-C_4H_9NC]^+$ 587 460 $[M - CO - t - C_4 H_9 NC - I]^+$ 543 [M---CO---I]+ 487 $[M-CO-I-Me_2C=CH_2]^+$ 460 $[M-CO-I-Me_2C=CH_2-HNC]^+$ $[M-CO-I-t-C_4H_9NC-C_2H_5]^+$ 431 $[M-CO-I-t-C_4H_9NC-C_2H_5-C_2H_5NC]^+$ 376

Table 4. Ma	ss spectral data	a of 2 , 3	, 5 and 6
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poses under EI conditions with elimination of CO and formation of $[(\eta^5 - C_5H_5)(I)_2(t-C_4H_9NC)W \equiv CNEt_2]^+$ (m/z = 670), the molecular ion of 2. This ion could not be detected in the mass spectrum of 2 under EI conditions.

CONCLUSION

Starting from $(\eta^5 - C_5 H_5)(CO)_2 W \equiv CNEt_2$, the precursor of $(\eta^5 - C_5 H_5)(I)_2(CO)W \equiv CNEt_2$, and $(\eta^{5}-C_{5}H_{5})(t-C_{4}H_{9}NC)(CO)W \equiv CNEt_{2}$, we were able to isolate by high yield methods, neutral and cationic cyclopentadienyl-substituted tungsten carbyne complexes containing isocyanide ligands. The oxidative decarbonylation of the electron-rich complex $(\eta^{5}-C_{5}H_{5})(t-C_{4}H_{9}NC)(CO)W \equiv CNEt_{2},$ enabled us to synthesize $[(\eta^5-C_5H_5)(I)(t-C_4H_9NC)]$ (CO)W \equiv CNEt₂]⁺I⁻, the first cationic diethylaminocarbyne complex of high-valent tungsten containing a carbonyl ligand. Its decarbonylation leads to the first neutral, carbonyl-free diethylaminocarbyne complex of high-valent tungsten. Based upon the spectroscopic data, the mass spectral data and the conductivity measurements, we suggest a neutral structure with a *cis*-orientation of the two iodide ligands for 2 and an ionic structure with a trans-orientation of the two isonitrile ligands for 3. In both molecules an iodide ligand, acting as a π -donor, is located in the *trans*-position relative to the carbyne ligand. Therefore, we assume that the same orientation is retained in the ionic compound 6, although we cannot exclude stereoisomers with a different orientation.

The new complexes are useful starting materials for the investigation of isonitrile carbyne coupling reactions induced by electrophiles or reducing agents.¹⁷

EXPERIMENTAL

 KC_5H_5 was prepared from KH and C_5H_6 in THF. $(\eta^5 - C_5 H_5)(I)_2(CO)W \equiv CNEt_2$ and mer-I(t- $C_4H_9NC_3(CO)W \equiv CNEt_2$ were synthesized as described previously.^{9,12} $t-C_4H_9NC$ was distilled and stored under nitrogen. All operations were carried out under nitrogen or argon atmospheres using Schlenk tube techniques. The solvents were dried by standard methods (n-pentane, toluene, Et₂O and THF over Na; CH_2Cl_2 over P_4O_{10} and Na/Pb alloy). The Al₂O₃ used for filtration (Merck Darmstadt, neutral, activity I, 0.063-0.2 mm) was degassed and dried at room temperature in vacuo, and then saturated with nitrogen. Elemental analyses were determined by the Microanalytical Laboratory of this department. IR spectra were measured with a Nicolet DX5 FT spectrophotometer,

NMR spectra with a Jeol GX 270 FT instrument and mass spectra with a Varian MAT CH7 spectrometer using EI conditions for 2, 5 and 6 and the SIMS method for 3. Conductance measurements were carried out as described previously.^{6-8,16}

$(\eta^{5}-C_{5}H_{5})(I)_{2}(t-C_{4}H_{9}NC)W \equiv CNEt_{2}$ (2)

A purple solution of 1 (180 mg, 0.29 mmol) and t-C₄H₉NC (0.04 cm³, 0.35 mmol) in THF (60 cm³) was heated for 1 h at 50°C until the v(C=O) band in the IR spectrum of 1 at 2000 cm⁻¹ disappeared. The red-purple solution was reduced in volume and an Et₂O-pentane mixture (1:2) was added. The supernatant, almost colourless solution was removed and the purple, microcrystalline solid dried *in vacuo* (190 mg, 97% relative to 1). (Found : C, 27.0; H, 3.5; I, 38.1; N, 4.2; W, 28.2. C₁₅H₂₄I₂N₂W (670.03) requires: C, 26.9; H, 3.6; I, 37.9; N, 4.2; W, 27.4%.)

$[(\eta^{5}-C_{5}H_{5})(I)(t-C_{4}H_{9}NC)_{2}W \equiv CNEt_{2}]^{+}I^{-}$ (3)

A red-purple solution of 2 (140 mg, 0.21 mmol) and t-C₄H₉NC (0.032 cm³, 0.28 mmol) in THF (50 cm³) was refluxed for 5 h. The colour of the solution turned brown-yellow. The solvent was reduced in volume and *n*-pentane was added. The supernatant light brown solution was decanted and the yellow, microcrystalline solid dried *in vacuo* (140 mg, 89% relative to 2). (Found : C, 31.9; H, 4.5; I, 32.6; N, 5.5; W, 24.6. C₂₀H₃₃I₂N₃W (753.16) requires : C, 31.9; H, 4.4; I, 33.7; N, 5.6; W, 24.4%.)

$$(\eta^{5}-C_{5}H_{5})(t-C_{4}H_{9}NC)(CO)W \equiv CNEt_{2}$$
 (5)

A mixture of 4 (280 mg, 0.42 mmol) and KC₅H₅ (0.70 mmol) was refluxed in THF (60 cm³) for 6 h. The solvent was then evaporated *in vacuo* and the residue extracted with Et₂O (3×30 cm³). The extracts were filtered through Al₂O₃ (2×3 cm) and the solvent removed *in vacuo* to give a yellow oil. Upon cooling a saturated solution of the yellow oil in *n*-pentane to -78° C, yellow crystals of **5** were obtained, which melt below room temperature (150 mg, 81% relative to **4**). (Found: C, 43.0; H, 5.4; N, 6.2. C₁₆H₂₄N₂OW (444.23) requires: C, 43.3; H, 5.4; N, 6.3%.)

 $[(\eta^{5}-C_{5}H_{5})(I)(t-C_{4}H_{9}NC)(CO)W \equiv CNEt_{2}]^{+}I^{-}$ (6)

To a yellow solution of 5 (110 mg, 0.25 mmol) in CH_2Cl_2 (30 cm³) was added at $-30^{\circ}C$, a purple solution of I_2 (62 mg, 0.24 mmol) in CH_2Cl_2 (20 cm³). The colour of the iodine solution disappeared immediately and the reaction solution turned first to red and then, upon warming up to room temperature, to orange. The solvent was reduced in volume *in vacuo* and an Et₂O-pentane mixture (1:2) was added. The supernatant, almost colourless liquid was decanted, and the microcrystalline, orange residue dried *in vacuo* (165 mg, 95% relative to 5). (Found: C, 27.6; H, 3.5; I, 36.1; N, 4.0; O, 2.3; W, 26.5. $C_{16}H_{24}I_2N_2OW$ (698.04) requires: C, 27.5; H, 3.5; I, 36.4; N, 4.0; O, 2.3; W, 26.3%.)

$(\eta^{5}-C_{5}H_{5})(I)_{2}(t-C_{4}H_{9}NC)W \equiv CNEt_{2}(2)$ from 6

An orange suspension of 6 (140 mg, 0.20 mmol) in THF (50 cm³) was refluxed for 1.5 h. Upon warming, 6 dissolved in THF to give first an orange solution, which then changed colour through red to red-purple. When all of 6 had been consumed (monitoring by IR) the solution was concentrated *in vacuo* and an Et₂O-pentane mixture (1:2) was added. The supernatant liquid was decanted and the microcrystalline, purple precipitate dried *in vacuo* (130 mg, 97% relative to 6).

2 was characterized by the ¹H NMR and IR spectra.

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