1,2 and 1,6 Additions of Lithium Reagents to γ-Methylenepyran Fischer-Type Carbene Complexes; Evolution of the 1,2 and 1,6 Adducts to Unsaturated Carbene Complexes Indirectly Stabilized by a Heteroatom, and to Pyranylidene Carbene Complexes

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1,2 and 1,6 additions of lithium reagents to γ-methylenepyran Fischer-type carbene complexes are described. The 1,2 adducts obtained from alkynyllithium addition evolve by a 1,3 shift of the $W(CO)_5$ fragment to give allenyltungsten carbonyl intermediates. Reaction with degassed water affords unsaturated carbene complexes indirectly stabilized by a heteroatom. The 1,6 anionic addition products are quenched by H_2O at low temperature to give α,δ-unsaturated carbene complexes. On warming, an evolution occurs leading to new pyranylidene carbene complexes.

Introduction

Due to the important role played in organic synthesis by Michael-type addition to electron deficient carbon-carbon double bonds, the reactions of various nucleophilic reagents including nitrogen nucleophiles, oxygen nucleophiles, phosphorus nucleophiles and carbon nucleophiles with α,β-alkenyl and alkynylcarbene complexes have been reported.[1,2] These complexes can be considered as equivalent to α,β-unsaturated esters and amides. However the presence of the metal carbonyl fragment introduces several differences in reactivity and the origin of the 1,2 and 1,4 selectivity of this class of reaction remains unknown. Temperature,[1e–3] the nature of the nucleophile[1e] and the metal,[2c,2e] and steric effects[1e,1a] have been proved to have an influence on the chemoselectivity.

In contrast to their 1,4 counterparts, the 1,6 addition of nucleophilic reagents to unsaturated carbene complexes has been neglected. However it has been found recently that a bulky alkoxy group in phenylcarbene complexes inhibits nucleophilic attack at the carbenic carbon and allows the observation of unusual 1,4 and 1,6 additions of secondary alkyllithiums to the aromatic center.[4]

We have recently described the reaction of pyrylium salts with carbanions of Fischer-type carbene complexes.[5a] The use of unsubstituted γ-pyrylium salts led to new unsaturated γ-methylenepyran Fischer-type carbene complexes (Scheme 1).[5b]

These compounds possess a pyrylium character and present three potential active sites towards nucleophiles, hence they should allow the unprecedented observation of 1,6 conjugate-type addition to α,δ-dialkenyl carbene complexes. We have previously shown that, at room temperature, amines react with these substrates by the well-known 1,2 addition elimination process, leading to γ-methylenepyran aminocarbene complexes.[5b]

We wish to report herein the 1,2 and 1,6 additions of lithium reagents to these complexes. We have shown that the 1,6 addition is temperature dependent leading to the adduct or, after ring opening and a subsequent cyclization, to pyranylidene complexes. On the other hand we have observed that alkynyllithium reagents give 1,2 addition to afford, after a 1,3 shift of the $W(CO)_5$ group, unsaturated carbene complexes indirectly stabilized by a heteroatom.[6] A recent report in this field prompted us to disclose our own observations.[7]

Results and Discussion

Treatment of the methylenepyran complex **1** with *n*Buli in THF at –80 °C provided, after hydrolysis and purification by chromatography, a 2:1 mixture of the red diastereoisomeric 1,6 adducts **3a** and **4a** (42% yield). (Scheme 1). Adding *n*Buli at –80 °C and warming the solution to room temperature led, after a chromatographic separation on silica gel plates, to the pyranylidene carbene complexes **7a** (32%) and **8a** (32%).[8] A 9% yield of a mixture of **3a** and **4a** was also isolated. A similar trend was observed with the chromium complex **2**. In this case hydrolysis performed at –60 °C afforded the α,δ-unsaturated carbene complex **5** (47% yield) as the sole isomer, together with the pyranylidene

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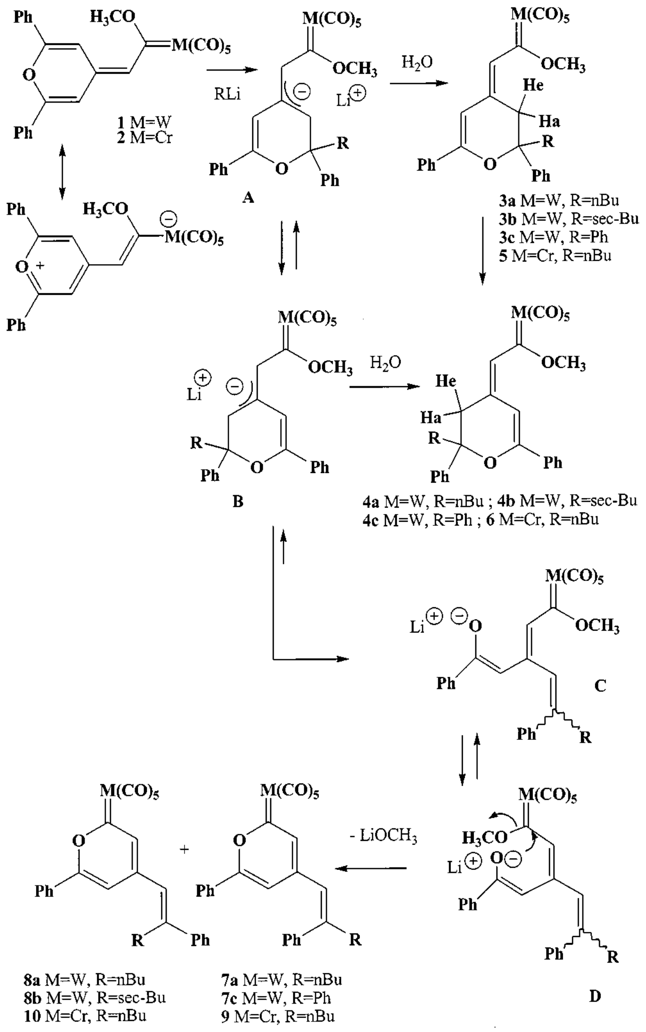


Scheme 1. Reaction of lithium reagents to **1** and **2**

complexes **9** (16% yield) and **10** (16% yield). Again, action of water at room temperature gave only **9** and **10** (in 24% and 11% yield, respectively). In this case the formation of unidentified nonorganometallic products was observed by thin layer chromatography.

Sec-butyllithium similarly reacted with **1**. Hydrolysis performed at –70 °C allowed the obtention of **3b** (mixture of diastereoisomers, 15% yield) and **4b** (mixture of diastereoisomers, 10% yield) together with a small quantity of **8b** (7% yield). Hydrolysis performed at room temperature afforded **8b** in 35% yield as a single isomer. Finally, with PhLi and **1**, the reaction required higher temperatures. Hydrolysis performed at –20 °C gave a 1:1 mixture of **3c** and **4c** (11% yield) and the pyranylidene complex **7c** (40% yield). In this case a 10% yield of **1** was recovered. Quenching the reaction mixture with water at room temperature gave **7c** in 42% yield.

The pyranylidene carbene complexes **7, 8, 9** and **10** are thought to arise from a nucleophilic 1,6 addition of lithium reagents to form the allylic anions **A** and **B** (Scheme 1), followed by a ring opening elimination step leading to the dienolate anions **C** and **D**. Finally, a ring closure reaction involving the negative oxygen atom and the carbenic carbon occurs, a process well documented in the chemistry of Fischer-type carbenes.[1g,8,9] In the case of the addition of *n*-butyllithium, careful monitoring of the reaction mixture by thin layer chromatography revealed the rapid formation of the allylic anion **A** (detection of **3a** as the sole isomer at the beginning of the reaction) which slowly equilibrates to **B** (detection of a mixture of **3a** and **4a** at the end of the reaction). This suggests the assistance of the carbenic fragment in the addition of lithium reagents. The stereochemical assignment of the obtained 1,6 adducts **3,5–4,6** was determined by ^{1}H NMR spectroscopy. In isomers **3–5** (Scheme 1), the equatorial hydrogen is shifted to low field as a consequence of the presence of the carbenic fragment. [for example, ^{1}H NMR ($CDCl_3$) **3a:** $\delta = 2.89$ (d, $J = 16$ Hz, H axial), 3.50 (d, $J = 16$ Hz, H equatorial); **4a:** $\delta = 2.81$ (d, $J = 16$ Hz), $\delta = 2.93$ (d, $J = 16$ Hz)].

The configuration *Z*/*E* of the pyranylidene complexes which originates from the ring opening elimination step (Scheme 1) was determined by X-ray crystallography carried out on **7a** (Figure 1 and by NMR spectroscopy. The hydrogens of the pyran ring are shifted to low field in the *Z* isomer because of the proximity of the phenyl group [for example, ^{1}H NMR ($CDCl_3$) **8a:** $\delta = 6.55$ and 7.60; **7a:** $\delta = 7.20$ and 8.05]. In addition, we have observed that the complexes **7a** and **9** isomerize slowly in solution to the more stable isomers **8a** and **10**.1

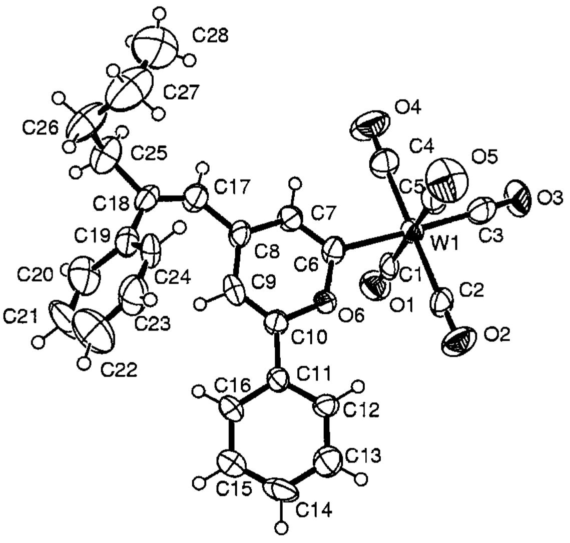
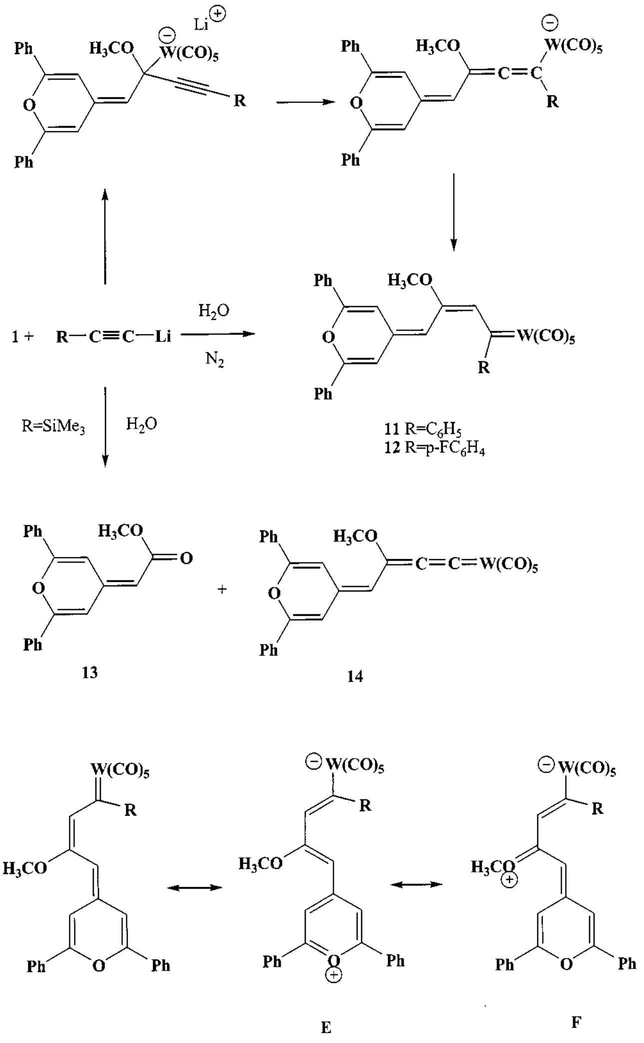


Figure 1. ORTEP view of the molecular structure of **7a** ($C_{28}H_{22}O_6W$); thermal ellipsoids are drawn at the 50% probability level; selected bond lengths [Å]: W(1)–C(6) 2.203 (11), C(6)–C(7) 1.377 (16), C(7)–C(8) 1.373 (15), C(8)–C(9) 1.445 (16), C(9)–C(10) 1.344 (17), O(6)–C(10) 1.370 (13), O(6)–C(6) 1.366 (13), C(8)–C(17) 1.455 (16), C(17)–C(18) 1.295 (16); selected bond angles [deg]: O(6)–C(6)–W(1) 116.5 (8), C(7)–C(6)–W(1) 127.5 (9), C(8)–C(7)–C(6) 125.1 (11), C(7)–C(8)–C(9) 114.7 (11), C(7)–C(8)–C(17) 122.3 (11), C(9)–C(8)–C(17) 123.0 (11), C(10)–C(9)–C(8) 121.8 (11), C(9)–C(10)–O(6) 118.5 (11), O(6)–C(6)–C(7) 115.7 (10), C(18)–C(17)–C(8) 133.6 (13)

We next examined the reactivity of an alkynyllithium towards **1**. A dramatic change in reactivity was observed. Thus, with lithium phenylacetylide a clean reaction took place in THF at room temperature leading, after reaction with degassed water, to the carbene complex **11**, which is indirectly stabilized by a heteroatom (Scheme 2), in 54% yield. The 4-fluorophenyllithium acetylide lithium 4-fluorophenylacetylide reacted similarly. Complex **12** was obtained in 30% yield.



Scheme 2. Reaction of lithium acetylide to **1**

The formation of the carbene complexes **11,12** is best explained by the addition of the sterically less-crowded linear lithium acetylide reagent to the carbenic carbon (1,2 addition) followed by a 1,3 shift of the $W(CO)_5$ anionic fragment (Scheme 2). The allenyltungsten intermediate obtained is protonated with degassed water to give the unsaturated carbene complex **11–12**.

In a recent report, Barluenga et al. have described the reactivity of phenyllithium acetylide towards tungsten (aryl) complexes stabilized by a bulky menthyloxy group.[7] In this case the anionic allenyltungsten intermediate is trapped with methyl triflate to afford a mixture of a propargyl ether and, via an unstable, undetectable 2-phenylvinylcarbene, a Dötz reaction product. In **11,12**, the presence of the electron-donating methylenepyran and methoxy groups increases the stabilization of the carbenic fragment and allows the isolation of the unsaturated carbene complexes indirectly stabilized by a heteroatom.[10] An X-ray analysis performed on complex **11** confirms the electronic character of the heterocycle (Figure 2). In the crystal, the W–C distance (2.238 Å) proves to be significantly longer than the W–C distance found in $(CO)_5W{=}C(OMe)Ph$ (2.05 Å) and the C_{13}–C_6, C_{16}–C_{14}, C_{17}–C_{16} and C_{14}–C_{13} bond lengths (1.377 Å, 1.392 Å, 1.393 Å and 1.430 Å, respectively) suggest an important contribution of the resonance structure **E-F** (Scheme 2). Furthermore the pattern of alternating bond lengths between the carbon atoms of the oxygen heterocycle is not much different from that found in pyrylium salts substituted in the γ position by an electron-donating group.[11] In these salts the pyran resonance structure contributes to the valence bond description.2[11a]

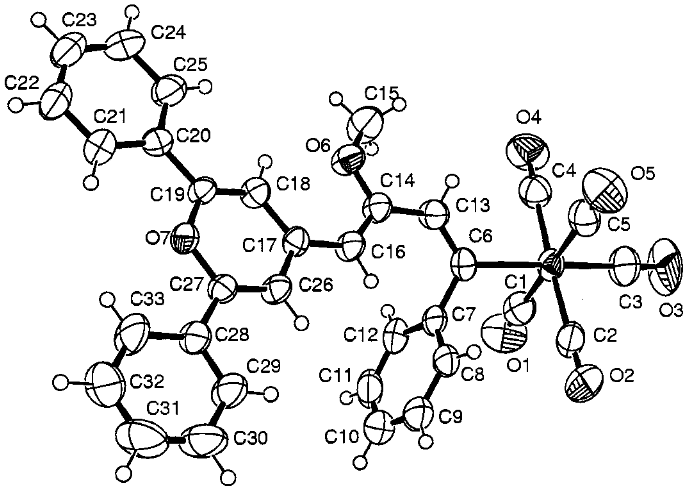
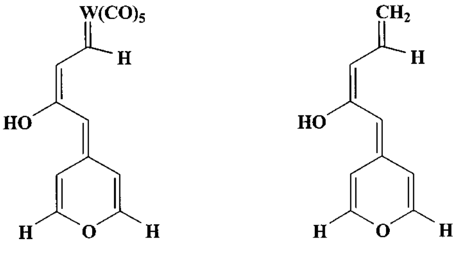


Figure 2. ORTEP view of the molecular structure of **11** ($C_{33}H_{22}O_7W$); thermal ellipsoids are drawn at the 50% probability level; selected bond lengths [Å]: W–C(6) 2.239 (6), C(6)–C(7) 1.479 (9), C(6)–C(13) 1.377 (9), C(13)–C(14) 1.430 (9), C(14)-0(6) 1.337 (8), C(14)–C(16) 1.392 (9), C(16)–C(17) 1.393 (8), C(17)–C(18) 1.426 (9), C(18)–C(19) 1.351 (8), O(7)–C(19) 1.353 (7), O(7)–C(27) 1.373 (7), C(27)–C(26) 1.338 (8); selected bond angles [deg]: C(13)–C(6)–W 123.3 (5), C(7)–C(6)–W 116.4 (4), C(6)–C(13)–C(14) 128.7 (6), O(6)–C(14)–C(16) 115.4, O(6)–C(14)–C(13) 119.1 (6), C(16)–C(17)–C(18) 127.0 (6), C(26)–C(17)–C(18) 113.9 (6), C(19)–C(18)–C(17) 122.3 (6), O(7)–C(19)–C(18) 120.0 (5), C(19)–O(7)–C(27) 121.0 (5), C(27)–C(26)–C(17) 123.3 (6)

The electronic connection between the metal center and the heterocycle has also been shown by an extended Hückel[12a,12b] MO study using the CACAO[13] package. Calculations have been carried out on a simplified model for **11**, labeled **11'** (Scheme 3), in which the phenyl and methyl groups have been replaced by hydrogen atoms (C–H = 1.08 Å; O–H = 0.96 Å). The conjugated system was considered perfectly planar so that the molecule has ideal C_s symmetry. The X-ray experimental distances of **11** were considered. In order to evaluate the role played by the metal center on the organic part of the molecule, calculations were also carried out on a model, labeled **15** (Scheme 3), in which the $W(CO)_5$ moiety was replaced by a CH_2 unit (C=

C= 1.35 Å), keeping the rest of the molecular structure unchanged.



11' 15

Scheme 3. Models **11′** and **15**

When going from **15** to **11’**, the C_{18}–C_{19} and C_{26}–C_{27} overlap populations are reduced (from 1.25 to 1.23, respectively). The C_{16}–C_{17} and C_{14}–C_{13} overlap populations are also reduced (from 1.09 and 1.07 to 1.04 and 0.97, respectively). On the other hand, the C_{14}–C_{16}, C_6–C_{13} and C_{14}–O_6 overlap populations increase (from 1.05, 1.02 and 0.67 to 1.10, 1.19 and 0.69, respectively). The net charge on O_7 is reduced from –0.57 to –0.53. These various population changes which were obtained considering the same frozen conjugated organic framework, are indicative of a significant participation in **11’** of the resonance formulae **E** and **F**. Moreover, the overlap population sequence along the C_{17}–C_6 chain in **11’** indicates a dominant character of **E** (Scheme 2). This situation is the consequence of a weak interaction between the π-type 5d occupied orbital of the $W(CO)_5$ fragment and the π LUMO of the organic moiety. Although this latter orbital is low-lying [due to significant 2pπ(O) participation], it is largely localized on the heterocycle (49%) with only 22% participation on C_6. Therefore, its overlap with the rather contracted d-type metallic orbital is weak and only 0.13 electrons are transferred into it. This result is consistent with a weak W–C_6 double bond character. As a consequence of this poor π-type interaction, the LUMO of the organic moiety is almost unperturbed and becomes the LUMO of **11’**.

Furthermore, calculations in which the $W(CO)_5$ unit in **11’** is replaced by an oxygen atom indicate comparable electronic effects between both types of substituents.

In addition, as anticipated with a ground state dominated by the mesomeric dipolar form, complex **11** exhibits a strong negative solvatochromic effect (λ CCl_4 672.9 nm, D.M.S.O., 616.5 nm).

As a conclusion of this part, it is also worth to point out the reaction of the trimethylsilyllithiumacetylide with **1**. As a result of the formal elimination of the $Si(Me)_3$ group, the allenylidene complex **13** is formed (37% yield)[14] together with the ester **14** as the main product (49% yield) (Scheme 2).

Conclusion

In summary, we have described the 1,2 and 1,6 addition of lithium reagents to γ-methylenepyran/Fischer type carbene complexes. Thus, while for alkyllithium and phenyllithium only the products from 1,6 conjugate addition are isolated, for alkynyllithium exclusive formation of 1,2 addition compounds is observed. In both cases, subsequent transformations of the adducts take place. Raising the temperature induces an unprecedented evolution of the 1,6 adducts to pyranylidene complexes. On the other hand the nonisolated propargylic 1,2 adducts evolve to an anionic allenyltungsten intermediate by a 1,3 $W(CO)_5$ shift. Hydrolysis of this species provides the formation of unsaturated carbene complexes indirectly stabilized by a heteroatom. The strong solvatochromic effect observed for the new donor -acceptor complex **11**[15] which crystallizes in a noncentrosymmetric group space induces us to investigate the N.L.O. properties.

Experimental Section

Physical Methods: ^{1}H NMR, ^{13}C NMR: Bruker 300 MHz, Bruker 500 MHz, TMS as internal standard. UV/Vis: Secomam 750. IR: Perkin–Elmer Spectrum 1000 FT-IR. Mass Spectra: MS/MS ZabSpec TOF micromass.

General Procedure for the Addition of Alkyllithium and Phenyllithium to 1 and 2. – Formation of the 1,6 Adducts 3, 4, 5 and 6 and of the Pyranylidene Complexes 7, 8, 9 and 10: To a solution of methylenepyran complex (5×10^{-4} mol) in THF was added, at –78 °C, under inert atmosphere conditions, a solution of the lithium reagent (5×10^{-4} mol). The reaction, controlled by TLC (petroleum ether/diethyl ether: 3/1) showed disappearance of the starting carbene complex. The reaction mixture was quenched with degassed water. Extraction with diethyl ether followed by chromatography on silica gel plates (elution: petroleum ether/diethyl ether 3:1) afforded the 1,6 adducts **3**, **5** and **4**, **6**.

When the reaction mixture was warmed to room temperature, the pyranylidene complexes **7**, **9** and **8**, **10** were obtained.

General Procedure for the Addition of Alkynyllithium to 1: To a degassed methylenepyran solution in THF (5.10^{-4} mol) was added alkynyllithium (obtained from alkynyl derivatives and *n*BuLi) at –60 °C. The mixture was warmed to room temperature, the color of the solution turning to red. Degassed water was then added and a green solution was obtained. Extraction with diethyl ether, drying over $MgSO_4$ and evaporation of the solvent gave complexes **11** or **12** as dark red solids.

Crystal Structure Analysis of 7a and 11: A crystal suitable for an X-ray diffraction study was mounted on a glass fiber and the X-ray data collected at room temperature on a Enraf–Nonius CAD4 diffractometer equipped with a graphite-monochromatized Mo-Kα (λ = 0.71073Å) radiation. The unit cell parameters were determined and refined from setting angles of 25 accurately centered reflections. Data were collected with the θ-2θ scan method. Intensities were corrected for Lorentz and polarization effects and a preliminary space group search performed with MolEN.[16] Both structures were solved by direct methods with SHELXS-97[17] and refined using full-matrix least-squares on F^2 using SHELXL-97.[18] The crystal data of the two compounds are presented in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supple-

Table 1. Crystal data and structure refinement for compounds **7a** and **11**

Identification code	**7a**	**11**
Empirical formula	$C_{28}H_{22}O_6W$	$C_{33}H_{22}O_7W$
Formula mass	638.31	714.36
Unit cell dimensions	a = 17.609(6) Å	a = 8.460(4) Å
	b = 6.692(7) Å	b = 11.948(4) Å
	c = 22.589(9) Å	c = 15.663(3) Å
	α = 90°.	α = 105.897(17)°
	β = 105.36(2)°	β = 95.00(3)°
	γ = 90°	γ = 90.23(4)°.
Volume	2567(3) Å^3	1516.3(10) Å^3
Z	4	2
Calculated density	1.652 g.cm^{-3}	1.565 g.cm^{-3}
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, P1bar
Index ranges	–21 h 20	0 h 10
	0 k 8	–14 k 14
	0 l 27	–19 l 19
θ range for data collection	1.31 to 26.13°	1.36 to 26.02°
Number of reflections with $I > 2\sigma(I)$	2642	4136
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0558, $wR2$ = 0.1157	$R1$ = 0.0440, $wR2$ = 0.0895
R indices (all data)	$R1$ = 0.1667, $wR2$ = 0.1510	$R1$ = 0.0921, $wR2$ = 0.1032

mentary publication no. CCDC-115637 for **7a** and CCDC-115638 for **11**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1FZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@CCDC.cam.ac.uk).

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