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Reaction of alkoxycarbene complexes of tungsten with 1,2-dihydroquinoline: single vs. double hydride transfers to the carbene–carbon: synthesis, X-ray structure and reactivity of a quinolinium ylide complex of tungsten pentacarbonyl

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Dedicated to Professor Ernst Otto Fischer, pioneer of Organometallic Chemistry, on the occasion of his 85th birthday

Abstract

The more stable dihydropyridine, 1,2-dihydroquinoline (**2**), reacts with carbene complex of tungsten $(CO)_5W{=}(OEt)Ph$ (**3**) to give the expected quinolinium complex **4**, fully characterized by an X-ray structure. By contrast, under the same conditions complex **7** $(CO)_5W{=}(OEt)Me$ led to the alkyltungstate **15** as the result of a double hydride transfer to the carbene–carbon. Complex **15** could be trapped by the enamine of morpholine and cyclohexanone and gave the addition product **14**. The quinoline in **4** is easily exchangeable by excess pyridine, via a dissociative mechanism, and gives the known pyridinium ylide complex **5**.

Keywords: Dihydropyridines; Carbenes; Quinolinium ylid; X-ray structure

1. Introduction

In a series of previous papers [1–5], we already described the interaction of dihydropyridines with alkoxycarbene complexes of chromium and tungsten. This led, via a two-step transformation to pyridinium ylide complexes as the result of a hydride transfer, an elimination of alcohol, and a re-addition of pyridine to the former carbene–carbon, according to Scheme 1.

A net re-aromatization of the dihydropyridines took place with transfer of both a hydride and a proton. The mechanism of the first step, the hydride transfer, could be assessed unambiguously by using instead of simple dihydropyridines, N-substituted dihydropyridines. This reaction led indeed to rather stable and useful, as far as their application to organic synthesis is concerned, pyridinium tungstates and chromates (Scheme 2) [6–12].

These transformations appeared to be of a general scope since the same type of complexes were obtained whatever the nature of the starting carbene complexes and of the dihydropyridines. Interest in this second type of transformation increased when we found that the reduction of the carbene complexes could be conducted in an enantioselective way by using chiral dihydropyridines [13]. There appeared therefore to be a good analogy between the reduction of carbene complexes and the biological and biomimetic reductions of carbonyl compounds by substituted dihydropyridines, the prosthetic group of NADH [14].

Up to now, we only examined the behaviour of chiral dihydropyridines derived from substituted pyridines, e.g. dihydronicotines, various *N*-alkyldihydropyridines bearing the stereogenic center in α to the nitrogen atom, and nicotinamides.

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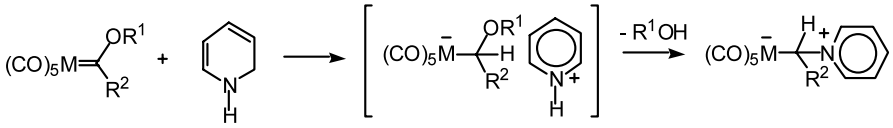
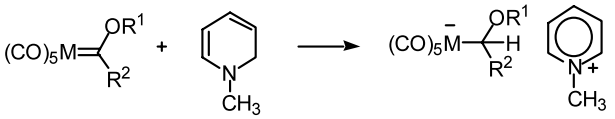


Scheme 1.



Scheme 2.

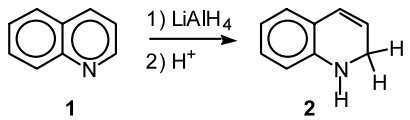
Since in the model enantioselective reduction of ketones, dihydropyridines fused to aromatic systems have been used very successfully for the preparation of chiral alcohols [15], we examined the behaviour of the structurally closest analogs, dihydroquinolines, in the reaction with carbene complexes.

The purpose of this paper is to describe the interaction of these specific dihydropyridines with two carbene complexes of tungsten, pentacarbonyl(ethoxy)phenyl carbene and pentacarbonyl (ethoxy)methyl carbene tungsten(0) [16], and to demonstrate that the course of the reaction is highly dependent on the structure of the carbene complex to be reduced.

2. Results and discussion

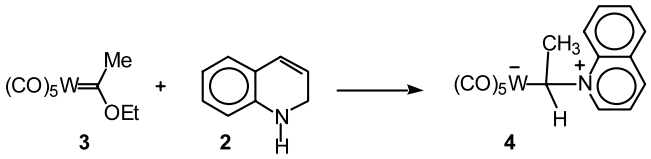
2.1. Reduction of complex *3* with dihydroquinoline: formation of the expected quinolinium ylide complex *4*

Quinoline **1** was reduced with $LiAlH_4$ according to Bohlmann [17] to afford ethereal stock solutions of dihydroquinoline **2**. According to the ^{1}H-NMR spectrum of the crude reaction product [18], the reduction took place as for pyridine giving however almost quantitatively 1,2-dihydroquinoline (**2**) which appeared to be much more stable than the corresponding dihydropyridines since it could be purified by silica gel chromatography.



1 **2**

Addition of one equivalent of an ethereal solution of 1,2-dihydroquinoline (**2**) to complex **3** at room temperature induced a rapid change of the colour from yellow to dark purple. After 1 h at room temperature, and according to TLC, some starting complex remained in the solution together with a new polar purple complex. After conventional workup followed by silica gel flash chromatography, the new complex (44% yield) could be easily separated and isolated as a solid, from the remaining starting complex (40%). Its NMR data were in agreement with structure **4**.



3 **2** **4**

The ^{1}H-NMR spectrum disclosed the two typical signals for an ethylidene group, at δ 2.53 ppm for a methyl group as a doublet ($J = 6.4$ Hz) and at δ 5.48 ppm, for a hydrogen, as a quartet ($J = 6.4$ Hz). Besides these, signals for the seven deshielded protons of the dihydroquinolinium nucleus from 8.96 to 7.67 ppm were present. The ^{13}C-NMR spectrum agreed also with such a structure since signals for two carbons, belonging, respectively, to a methyl group at δ 32.4 ppm, and to a methine at δ 50.1 ppm were present.

Whereas no difference in the chemical shifts of the methyl groups in **4** and **5** [2] was observed, the hydrogen atom on the former carbene–carbon suffered a significative upfield shift from 4.90 ppm in **5** to 5.48 ppm in **4**.

2.2. X-ray structure of complex *4*

Purple crystals, m.p. 97–99 °C, suitable for an X-ray analysis could be grown from mixtures of dichloromethane and hexanes. The crystallographic data corresponding to this complex can be found in Table 2 whereas the bond distances and bond angles are gathered in Table 1. A thermal ellipsoid plot of **4** appears in Fig. 1.

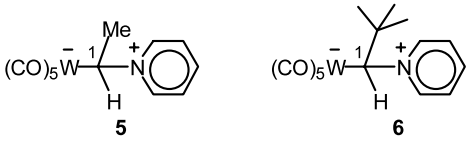
Of interest in this structure are the W–C(1) and C(1)–N bond distances and the geometry of the former carbene function with respect to the quinolinium group.

As far as the bond distances are concerned, they agree with those already observed for other complexes of this type, e.g. 6, W–C(1) being equal respectively to 2.366(6) Å for **4** and 2.369(6) Å for **6**, and C(1)–N(1), 1.488(8) and 1.504(8) Å.

As far as the geometry of the complex is concerned, the quinolinium ring is almost perpendicular to the W–C(1)–C(2) plane (95°) whereas an angle of 20° is observed between its plane and the plane of the four equatorial CO ligands.

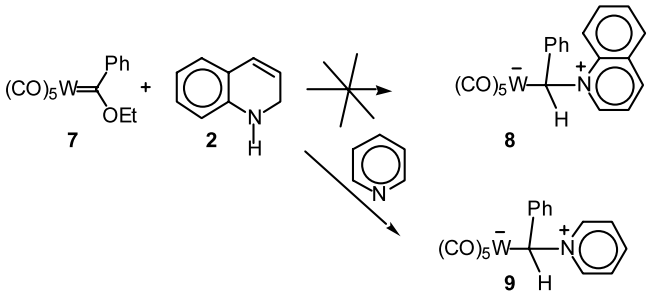
Table 1
Interatomic distances (Å) and bond angles (°) for $C_{16}H_{11}NO_5W$

Bond lengths			
W(1)–C(1)	2.366(6)	W(1)–C(12)	2.034(7)
W(1)–C(13)	2.012(7)	W(1)–C(14)	1.979(7)
W(1)–C(15)	2.015(8)	W(1)–C(16)	2.039(9)
O(1)–C(12)	1.137(9)	O(2)–C(13)	1.148(8)
O(3)–C(14)	1.151(9)	O(4)–C(15)	1.16(1)
O(5)–C(16)	1.13(1)	N(1)–C(1)	1.488(8)
N(1)–C(3)	1.336(8)	N(1)–C(11)	1.400(7)
C(1)–C(2)	1.53(1)	C(3)–C(4)	1.39(1)
C(4)–C(5)	1.35(1)	C(5)–C(6)	1.40(1)
C(6)–C(7)	1.42(1)	C(6)–C(11)	1.427(9)
C(7)–C(8)	1.34(1)	C(8)–C(9)	1.39(1)
C(9)–C(10)	1.38(1)	C(10)–C(11)	1.407(9)
Bond angles			
C(1)–W(1)–C(12)	95.2(3)	C(1)–W(1)–C(13)	95.0(2)
C(12)–W(1)–C(13)	87.9(3)	C(1)–W(1)–C(14)	173.2(3)
C(12)–W(1)–C(14)	88.5(3)	C(13)–W(1)–C(14)	90.8(3)
C(1)–W(1)–C(15)	87.0(3)	C(12)–W(1)–C(15)	175.6(3)
C(13)–W(1)–C(15)	88.1(3)	C(14)–W(1)–C(15)	89.6(3)
C(1)–W(1)–C(16)	84.3(3)	C(12)–W(1)–C(16)	91.0(4)
C(13)–W(1)–C(16)	178.7(3)	C(14)–W(1)–C(16)	90.0(3)
C(15)–W(1)–C(16)	93.0(4)	C(1)–N(1)–C(3)	120.4(5)
C(1)–N(1)–C(11)	120.4(5)	C(3)–N(1)–C(11)	119.1(6)
W(1)–C(1)–N(1)	111.8(4)	W(1)–C(1)–C(2)	114.5(4)
N(1)–C(1)–C(2)	110.8(6)	N(1)–C(3)–C(4)	122.9(7)
C(3)–C(4)–C(5)	120.1(7)	C(4)–C(5)–C(6)	119.7(6)
C(5)–C(6)–C(7)	122.0(7)	C(5)–C(6)–C(11)	119.6(6)
C(7)–C(6)–C(11)	118.4(6)	C(6)–C(7)–C(8)	120.8(7)
C(7)–C(8)–C(9)	120.8(7)	C(8)–C(9)–C(10)	121.2(7)
C(9)–C(10)–C(11)	119.5(6)	N(1)–C(11)–C(6)	118.7(6)
N(1)–C(11)–C(10)	122.0(6)	C(6)–C(11)–C(10)	119.3(6)
W(1)–C(12)–O(1)	176.2(7)	W(1)–C(13)–O(2)	178.6(6)
W(1)–C(14)–O(3)	177.2(8)	W(1)–C(15)–O(4)	175.8(9)
W(1)–C(16)–O(5)	177.8(10)		



2.3. Reduction of complex 7 with 1,2-dihydroquinoline: double hydride transfer

When the same reaction was carried out on complex **7**, an immediate fading of the red colour of the solution took place upon addition of the reducing agent, indicating that indeed a reaction took place.



However, according to TLC, no new complex such as **8** could be detected. That however the reduction took place as expected to give first the quinolinium tungstate and then, upon loss of ethanol, the alkylidene complex **11**, was confirmed by the following experience. Addition of dihydroquinoline to complex **7** in the presence of pyridine led, according to TLC, to a new complex. After workup and purification by silica gel chromatography, a yellow complex was obtained as a solid in 37% yield. Its physical data were in all respect in agreement with those

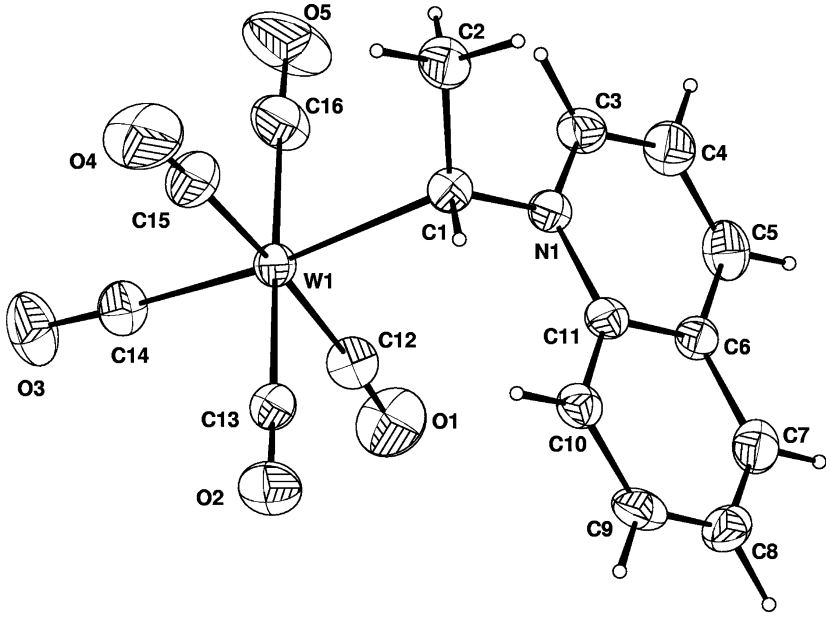
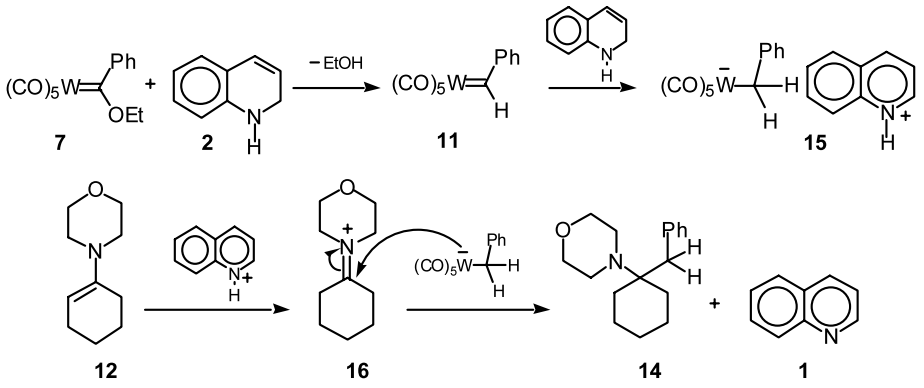


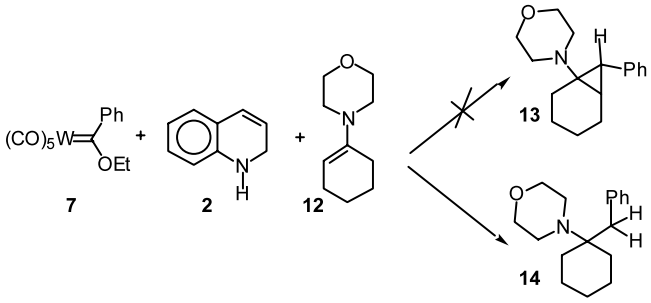
Fig. 1. Molecular projection of complex **4**.



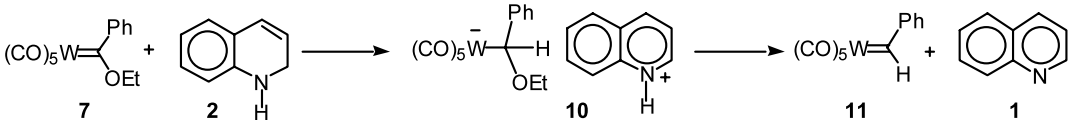
of complex **9** [19], the known pyridinium ylide complex arising from the interaction of the alkylidene complex **11** with pyridine [2]. Thus, complex **11** is able to react with pyridine but not with the more crowded quinoline.

2.4. Attempts to trap the alkylidene complex *11* with an enamine

We demonstrated [9–11] that pyridinium ylide complexes of the type **5** or **9** transfer smoothly their alkylidene moiety, at room temperature, to the carbon–carbon double bonds of enamines, giving aminocyclopropanes. This occurs probably via the alkylidene complexes upon loss of pyridine.



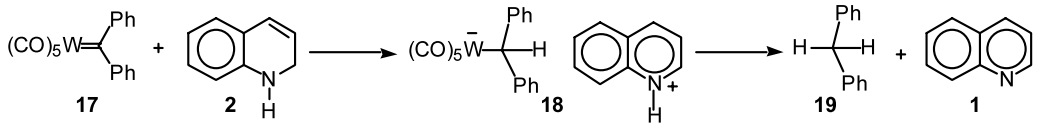
The formation of **14** can be rationalized in the following way:-reduction of **7** with dihydroquinoline leads via **11**–**15** [21], a new quinolinium tungstate, upon a second hydride transfer to the carbene carbon. This new complex is deprotonated by the enamine to the iminium tungstate **16** which can undergo an intramolecular addition reaction to give finally **14**.



We therefore attempted to trap the intermediate alkylidene complex **11** by carrying out the reaction in the presence of the enamine of cyclohexanone and morpholine **12**. However, much to our surprise, none of the expected cyclopropylamine **13** could be detected. Nevertheless, a new organic product was isolated: according to its NMR spectra, it results indeed from the addition of a benzyl group originating from **11**, to the enamine **12**, since signals for all the protons and carbons of the starting organic moieties could be assessed. Most characteristic, the ^{13}C-NMR spectrum disclosed, besides six methylene groups, a signal due to a quaternary carbon, at δ 58.1 ppm, and the ^{1}H-NMR spectrum, a singlet at δ 2.63 ppm for a methylene group. All these data agreed with structure **14** [20], the product resulting from the addition of a benzyl group to the α-carbon of the double bond of the enamine **12**.

2.5. Interaction of complex *17* with dihydropyridines

Confirmation that dihydropyridines can indeed reduce twice alkoxycarbene complexes via the related alkylidene complexes came from the interaction of complex **17** [22], a rather stable alkylidene complex of tungsten, with either dihydroquinoline or dihydropyridines. In both cases a fast change of colour from deep



red to light yellow was observed upon mixing of both compounds.

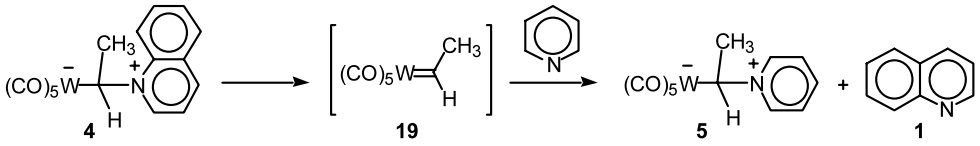
A new product, identified as diphenylmethane **19** according to its spectroscopic data, was isolated in 20% yield after silica gel chromatography: it results from the reduction of the starting complex **17** to the quinolinium tungstate **18** followed by protonation at the metal and reductive elimination.

This observation confirms that the reduction of alkylidene complexes is very fast and can compete favorably with the reduction of alkoxycarbene complexes and thus can explain the behaviour of complex **7** towards dihydroquinoline.

2.7. Kinetics and mechanism of the substitution reaction

In order to get an insight into the mechanism of the transformation of **4** into **5**, a plot of $\log c$, the concentration of the starting complex, vs. time, was drawn: this is linear. At the same temperature, the rate is independent of the concentration of the starting complex and the ratio **4**/pyridine. Therefore, the reaction follows first-order kinetics. The limiting step is therefore the elimination of quinoline from complex **4** with formation of the alkylidene complex **19** followed by a fast interaction of the latter with pyridine.

These results are also in agreement with previous



observations of this laboratory concerning the exchange of pyridine in complexes **9** and **21** with excess perdeuterated pyridine, the reaction being much slower for **21** (3 days) than for **9** (10 mn). Complex **20** could be isolated, after elimination of pyridine, and fully characterized by NMR spectroscopy [23].

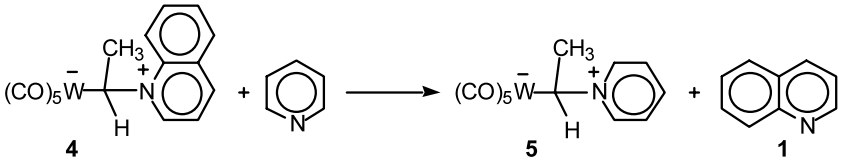
Further details about the kinetics of these and other substitution reactions involving ylid complexes will appear in a forthcoming paper.

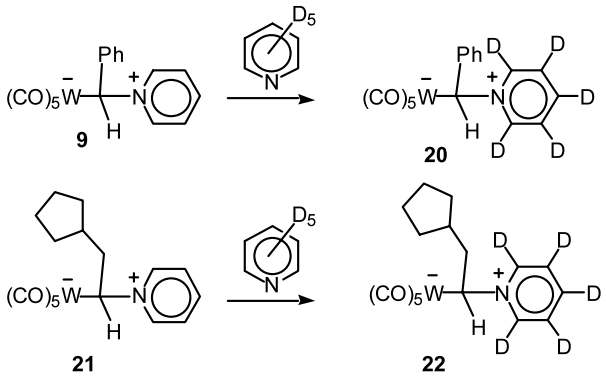
2.6. Behaviour of complex *4* towards pyridine: formation of the pyridinium ylid complex *5*

The behaviour of complex **7** towards dihydroquinoline provides direct evidence that, for steric or electronic reasons, the bond between the carbene–carbon of alkylidene complexes and quinoline is weaker than the corresponding bond in pyridinium ylid complexes. Exchange of quinoline with pyridine would therefore be very likely to occur. And this was indeed the case since addition of pyridine to methylene chloride solutions of complex **4** very rapidly led (in less than 1 h) to the pyridine ylid complex **5** with release of quinoline. Such an exchange could easily be monitored by ^{1}H-NMR spectroscopy since the signals of the alkylidene protons in **4** and **5** appear at quite different fields (4.88 for **5** vs. 5.48 ppm for **4**).

3. Conclusion

The most important result of the present paper, besides the formation of a new, very crowded pyridinium ylid complex, is the possibility which is given now to prepare directly, by the choice of simple dihydropyr-





idines, new tungsten ate complexes resulting from a double reduction reaction. The formation and reactivity of these complexes, which appears already herein, will be taken into advantage to be extended to more elaborate alkoxycarbene complexes.

4. Experimental

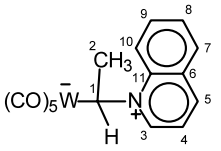
All reactions were performed under an inert atmosphere of argon. The solvents were dried by distillation over the following drying agents prior to use and were transferred under argon: Et_2O, THF (Na/benzophenone), CH_2Cl_2 (P_4O_{10}), toluene (Na). Chromatography was carried out on Merck silica gel, 70–230 mesh. NMR spectra were recorded on Bruker AC 200 or ARX 400 spectrometers; chemical shifts (δ) are given in parts per million relative to TMS and coupling constants (J) in hertz. HRMS measurements were carried out on a JEOL MS 700 instrument (70 eV). Melting points were determined on a Reichert instrument.

4.1. Preparation of dihydroquinoline 2

1,2-Dihydroquinoline was prepared from quinoline and $LiAlH_4$ according to the literature and isolated after silica gel chromatography as a white solid in 95% yield.

4.2. Reaction of complex 3 with dihydroquinoline 2: formation of complex 4

To a solution of carbene complex **3** (0.8 g, 2.06 mmol) in diethylether (50 ml), was added by syringe dihydroquinoline **2** (0.4 g, 1.1 equivalent) at room temperature (r.t.) The reaction mixture was allowed to stir until complete disappearance of the starting material (10–20 min). Flash chromatography on silica gel gave with hexanes as eluent the starting carbene complex (0.32 g, 0.82 mmol, 40%) and with dichloromethane as the eluent the ylide complex **4** in 44% yield (430 mg, 0.89 mmol) as a purple solid, m.p. 97–99 °C. Anal. Calc. for $C_{16}H_{11}NO_5W$, C, 39.94; H, 2.30; N, 2.91. Found: C, 39.29; H, 2.41; N, 3.01%. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 8.96 (d, 1H, $J = 5.6$ Hz, H-3), 8.58 (d, 1H, $J = 9.2$ Hz, H-5), 8.30 (d, 1H $J = 8.1$ Hz, H-7), 8.06–8.03 (m, 2H, H-4 and H-10), 7.79 (dd, 1H, $J = 7.4$–7.4 Hz, H-8), 7.67 (dd, 1H, $J = 7.4$–7.4 Hz, H-9), 5.48 (q, 1H, $J = 6.4$ Hz, H-1), 2.53 (d, 3H, $J = 6.4$ Hz, H-2). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 202.0 (*trans* CO), 198.0 (*cis* CO), 138.7–120.2 (qC and arom CH), 50.1 (C-1), 32.4 (C-2).

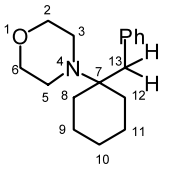


4.3. Reaction of carbene complex 7 with dihydroquinoline in the presence of pyridine: formation of complex 9

To a solution of 500 mg (1.09 mmol) of carbene complex **7** (0.5 g;1.09 mmol) in diethylether (100 ml) at r.t., was added by syringe dihydroquinoline **2** (0.15 g, one equivalent). The reaction mixture was allowed to stir for 15 min; then pyridine (0.09 g, one equivalent) was added. After 15 h at r.t., the solvent was evaporated under vacuum and the residue was chromatographed on silica gel, giving a yellow solid (0.2 g, 0.4 mmol) in 37% yield the spectroscopic data of which agreed with those of complex **9**.

4.4. Reaction of carbene complex 7 with dihydroquinoline 2 in presence of the enamine 12: formation of 14

To a solution of 500 mg (1 mmol) of carbene complex **7** (0.5 g, 1.09 mmol) in dichloromethane (50 ml) was added dihydroquinoline **2** (0.52 g, 4 mmol) at r.t. After total consumption of the starting material, 4-cyclohex-1-enyl-morpholine (**12**) (0.608 g, 4 mmol) was added and the reaction stirred for 15 h. After evaporation of the solvent under vacuum followed by silica gel chromatography of the residue the adduct **14** was obtained as a white solid (121 mg, 0.468 mmol, 46.8%), m.p. 63–65 °C [20].



4.4.1. 4-(2-Benzyl-cyclohexyl)-morpholine

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.12 (m, 5H, aromatic), 3.75 (t, 4H, $J = 4.3$ Hz, H-2 and H-6), 2.66 (t, 4H, $J = 4.3$ Hz, H-3,5), 2.63 (s, 2H, H-13), 1.78–1.75 (m,

Table 2
Crystal data for $C_{16}H_{11}NO_5W$

F_w	481.12
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.005(2)
b (Å)	22.957(3)
c (Å)	9.332(1)
α (°)	90
β (°)	110.22(1)
γ (°)	90
V (Å^3)	1609.2(5)
Z	4
Linear absorption coefficient μ (cm^{-1})	73.5
Density ρ (g cm^{-3})	1.99
Diffractometer	CAD4 Enraf-Nonius
Radiation	Mo–K$_\alpha$($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345tg\theta$
θ Limits (°)	1–28
Temperature of measurement (K)	295
Octants collected	0, 10; 0, 30; −12, 11
Nb of data collected	4256
Nb of unique data collected	3878 ($R_{int} = 0.03$)
Nb of unique data used for refinement	2481 $(F_o)^2 > 3\sigma(F_o)^2$
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0282
R_w [a] $= [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.0357
S	1.10
Extinction parameter	None
Nb of variables	209
$\Delta\rho$ min (e Å^{-3})	−0.57
$\Delta\rho$ max (e Å^{-3})	0.66

[a] $w = w'[1-((\|F_o\|-\|F_c\|)/6\sigma(F_o))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with three coefficients 5.90, −2.34 and 4.31 for a Chebyshev Series, for which X is F_c/F_c (max).

2H), 1.68–1.56 (m, 3H), 1.32–1.29 (m, 2H), 1.15–1.08 (dt, 2H, $J = 13.5$–3.2 Hz), 1.02–0.97 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.4 (qC), 130.8–125.8 (Cq and aromatic carbons), 68.2 (C-2 and C-6), 58.1 (C-7), 44.6–39.5–32.0–25.9–20.7.

4.5. Reaction of complex *17* with dihydroquinoline *2*: formation of diphenylmethane *19*

To a solution of carbene complex **17** (0.85 g, 1.7 mmol) in dichloromethane (50 ml) at −50 °C, was added dihydroquinoline **2** (0.25 g, 1.9 mmol). After stirring at r.t. for 12 h, the solvent was evaporated under vacuum and the residue chromatographed on silica gel. Elution with hexanes gave a liquid (0.051 g, 20%) the NMR data of which agreed fully with those of diphenylmethane **19**.

4.6. Kinetic measurements

All the data were obtained by ^{1}H-NMR: Complex **4** (5.4 mg) was dissolved in $CDCl_3$ (400 μl). Pyridine (4 μl) was then added and the evolution of the reaction followed by NMR. The ratio complex **4**/complex **5** was obtained by integrating the signals of CH-1 at 5.5 and 4.88 ppm.

Similar plots were obtained by modifying either the concentration of the starting complex or the concentration of pyridine.

4.7. Structural determination of complex 4

Intensity data were collected at r.t. on an Enraf-Nonius CAD4 diffractometer using Mo–K$_\alpha$ radiation. Accurate cell dimensions and orientation matrices were obtained from least-square refinements of the setting angles of 25 well-defined reflections. No significant decay in the intensity of two standard reflections was observed during the course of the data collections. Crystal data, collection parameters and other significant details are listed in Table 2.

The usual corrections for Lorentz and polarization effects were applied. Computations were performed by using CRYSTALS [24]. Scattering factors and corrections for anomalous dispersion were taken from the International Table for X-ray Crystallography [25]. The structures were resolved by direct methods (SHELXS) [26] and refined by least squares with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were introduced in calculated positions and only one overall isotropic displacement parameter was refined.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 202588 for compound **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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