Cyclopalladated Complexes Derived from Diphenylhydrazones and their Transmetallation Reaction

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Abstract. Mononuclear cyclopalladated complexes of type $PdCl(Ph_2N\text{-}N{=}CR_1\text{-}C\text{-}R_2{=}N\text{-}NPh_2)$, where $R_1{=}R_2{=}H$ (**2a**), $R_1{=}R_2{=}CH_3$ (**2b**), and $R_1{=}H$, $R_2{=}CH_3$ (**2c**) were synthesized by the reaction of palladium chloride and hydrazones. Additionally, the reaction of the complex **2c** towards lithium phenylacetylide was studied, giving $Ph_2N{-}N{=}C(CH_3){-}CH{=}N{-}N(Ph)(o\text{-}C_6H_4{-}C{\equiv}C{-}Ph)$ (**3**) . The complexes **2a**-**2c** and compound **3** were characterized by IR, Mass, ^1H, ^{13}C, and 2D NMR spectroscopy. X-ray structure of complex **2c** was also determined.

Keywords: Palladium; Cyclopalladated complexes; Hydrazones; Transmetallation; Crystal structure

Cyclopalladierte Komplexe durch Transmetallierungsreaktion mit Diphenylhydrazonen

Inhaltsübersicht. Einkernige Palladiumkomplexe der Art $PdCl(Ph_2N\text{-}N{=}CR_1\text{-}C\text{-}R_2{=}N\text{-}NPh_2)$, mit $R_1{=}R_2{=}H$ (**2a**), $R_1{=}R_2{=}CH_3$ (**2b**) und $R_1{=}H$, $R_2{=}CH_3$ (**2c**) wurden durch Reaktion von Palladiumchlorid mit Hydrazonen dargestellt. Zusätzlich wurde die Reaktion des Komplexes **2c** mit Lithiumphenylacetylid untersucht, die $Ph_2N{-}N{=}C(CH_3){-}CH{=}N{-}N(Ph)(o\text{-}C_6H_4{-}C{\equiv}C{-}Ph)$ (**3**) ergab. Die Komplexe **2a-c** und die Verbindung **3** wurden durch IR-, Massen-, ^1H-, ^{13}C- und 2D-Spektroskopie charakterisiert. Eine Röntgenstrukturanalyse von **2c** wurde ebenfalls vorgenommen.

Introduction

Palladium complexes have been the subject of interest due to their applications in organic synthesis [1, 2]. Various cyclopalladated complexes with tridentate N-donor ligands e.g. azines, oximes [3], hydrazones [4−11] have been reported affording to mononuclear structures, while tridentate imines present dinuclear as well as mononuclear structures [12, 13].

It has been reported earlier that cyclopalladated complexes show reactivity towards alkynes, alkenes, CO and isocyanides [1, 2, 14]. Mono-, bis- and tris-insertions of alkynes in cyclopalladated complexes are known in literature [2, 15, 16]. Reports on insertion of alkynes into the $\sigma(Pd\text{-}C_{sp2,ferrocene})$ bond show different reactivity to that of $\sigma(Pd\text{-}C_{sp2,aryl})$ bond [17−20].

We report herein, the synthesis and characterization of some new palladium complexes derived from N,N-diphenylhydrazones. The transpalladation of these complexes on reaction with lithium phenylacetylide was also studied.

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Results and Discussion

The ligands **1a**−**1c** were prepared by condensation reaction of *N,N*-diphenyl hydrazine with the corresponding 1,2-dicarbonylic compounds. The reaction of **1a**−**1c** with $PdCl_2$ afforded cyclopalladated complexes **2a**−**2c** (Scheme 1).

The IR spectra of ligands **1a**−**1c** show an absorption band at 1590cm^{-1} corresponding to ν(C=N) vibration. This band shows a slight shift (~2−5 cm^{-1}) to higher frequency after cyclopalladation. The FAB^+ mass spectra show molecular ions m/z = 530 and m/z = 544 for **2a** and **2c** respectively. A molecular ion peak could not be observed for compound **2b**, but ion peak observed at m/z = 523 represents the molecular ion with loss of a chlorine atom.

The ^1H and ^{13}C data are reported in Table 1. The assignments of the parameters are based on 2D experiments.

The ^1H spectra of **2a**−**2c** show upfield shifts for the aromatic protons with respect to free ligands **1a**−**1c**. Proton present at *ortho* position to the Pd-C bond (H-3) was strongly shielded after cyclopalladation in comparison to protons present at *meta* and *para* positions.

Similar to ^1H NMR spectra, ^{13}C NMR data of **2a**−**2c** reveal that the aromatic carbon atoms for the cyclopalladated ring are shifted to higher frequencies in comparison to the free ligand.

The molecular structure of **2c** was established by single-crystal X-ray diffraction analysis. Structural data, selected bond lengths and angles are given in Table 2 and 3, respectively. The structure of **2c** shows that the palladium atom is linked to four atoms and the bond angles at the palladium

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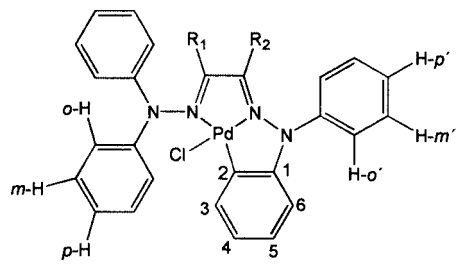
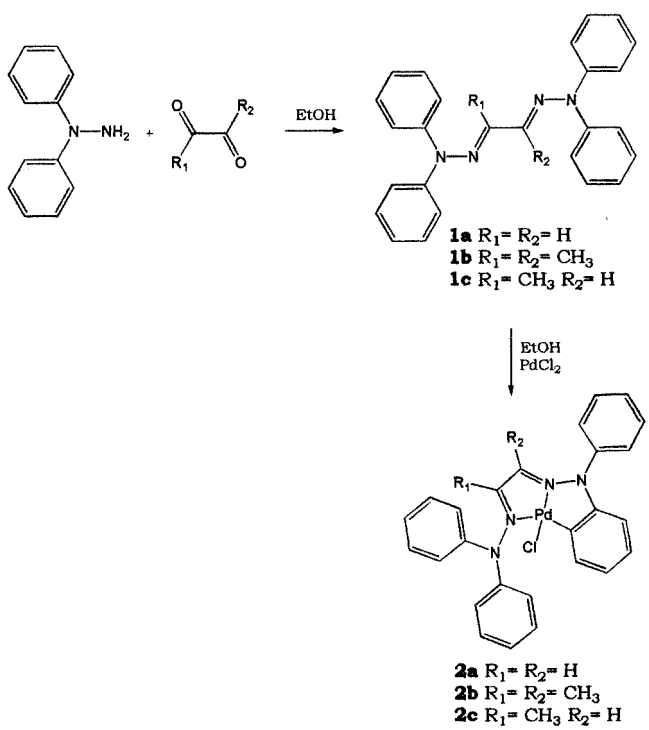
Table 1 ^{1}H and ^{13}C NMR data for **2a**−**2c**

	CH_3	H-3	H-4	H-5	H-6	H-*o*′	H-*m*′	H-*p*′	H-*o*	H-*m*	H-*p*	HC=N
2a		5.79(1H, dd,J=7.2)	6.63(1H, J= 7.1)	t,6.77(1H, J=7.1)	t,7.56 (1H, dd,J=7.7, 1.7)	7.16-7.63(17H, m)	7.16-7.63(17H, m)	7.16-7.63(17H, m)	7.16-7.63(17H, m)	7.16-7.63(17H, m)	7.16-7.63(17H, m)	7.16-7.63(17H, m)
2b	1.65(3H,s)	2.01(3H,s)	6.11(1H, dd,J=7.7, 1.7)	6.67(1H, td,J= 7.7, 1.7)	6.75(1H, td, J=7.7, 1.7)	7.46(1H, dd,J=7.7, 1.7)	7.48-7.52(3H,m)	7.40(6H, t, J=7.7)	7.48-7.52(3H,m)	7.26(4H,d, J=7.1)	7.40(6H,t, J=7.7)	7.18(2H,t, J=7.1)
2c	1.90(3H,s)	5.81(2H, dd,J=7.7, 1.7)	6.68(1H, td,J= 7.7, 1.7))	6.75(1H, td, J=7.7, 1.7)	7.46(1H, dd,J=7.7, 1.7)	7.60-7.66(3H, m)	7.33-7.38(6H,m)	7.60-7.66(3H, m	7.24(4H,d, J=7.1)	7.33-7.38(6H,m)	7.15(2H,t, J=7.1)	6.34(1H,s)

	-C=N	C-1	C-2	C-3	C-4	C-5	C-6	C-*i*	C-*o*	C-*m*	C-*p*	C-*i*′	C-*o*′	C-*m*′	C-*p*′
2a	126.6	130.6	143.0	110.5		125.5	131.2		129.7	129.0	129.7		129.7	129.0	125.3
2b	174.4	136.1	148.9	112.6	122.7	125.5	146.0	159.1	130.3	128.1	130.3	159.1	148.9	129.5	125.0
2c	172.2	135.2	148.9	111.3	122.8	125.5	136.2	159.1	146.1	129.4	125.0	156.3	130.3	129.5	130.3



2a $R_1=R_2=H$
2b $R_1=R_2=CH_3$
2c $R_1=H$, $R_2=CH_3$



Scheme 1

Table 2 Crystallographic Data for Complex **2c**

Formula	$C_{27}H_{23}ClN_4Pd$
Formula Weight /g mol^{-1}	545.34
Crystal size (mm)	0.40 x 0.38 x 0.08
Color	purple
Crystal system	orthorhombic
Space group	*Pbca*
a /Å	17.748(2)
b /Å	14.582(2)
c /Å	18.190(2)
$\alpha=\beta=\gamma$ /°	90
V /Å^3	4794.8(10)
Z	8
$D_{calc.}$ /g cm^3	1.511
No. of collected reflections	3922
No. of independent reflections	3922
No. of observed reflections	3922
No. of parameters	298
R[a)]	0.0765
R_w[b)]	0.1361
GOF	0.991

a) $R=\Sigma||F_o| - |F_c|| / \Sigma|F_o|$, b) $R_w(F_o)^2 = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma wF_o^4]^{1/2}$

center range from 77.2(5) to 104.8(3)° giving rise to a distorted square planar structure (Figure 1). The Pd−N(5) bond length (1.96 (1) Å) *trans* to the chlorine, is slightly shorter than Pd−N(2) 2.19(1) Å distance, *trans* to the σ-Pd−C bond. This lengthening can be explained in terms of the *trans* influence of the σ-bonded carbon atom of the aryl group [5, 7]. It is important to notice, that the bond angle N(5)−N(6)−C(26) 117(1)° deviates from a previously re-

Table 3 Selected bond Lengths /Å and Angles /° of **2c**

Pd−C(27)	1.95(2)	C(27)−Pd−N(5)	81.8(6)
Pd−N(2)	2.19(1)	N(5)−Pd−N(2)	77.2(5)
Pd−N(5)	1.96(1)	N(5)−Pd−Cl	177.7(4)
Pd−Cl	2.29(4)	C(7)−N(1)−N(2)	114.3(10)
N(1)−N(2)	1.44(1)	C(3)−N(2)−Pd	111.8(9)
N(2)−C(3)	1.29(2)	N(2)−C(3)−C(4)	116.7(13)
C(3)−C(19)	1.45(2)	C(4)−C(3)−C(19)	117.5(13)
N(5)−N(6)	1.38(2)	C(4)−N(5)−N(6)	124.7(13)
N(6)−C(20)	1.43(2)	N(6)−N(5)−Pd	116.7(10)
N(6)−C(26)	1.39(2)	C(26)−C(27)−Pd	115.1 (14)
C(26)−C(27)	1.42(2)	N(6)−C(26)−C(27)	117.3(12)
C(4)−N(5)	1.34(2)	C(28)−C(27)−Pd	132.7(13)
C(3)−C(4)	1.44(2)	C(27)−Pd−N(2)	158.9(5)
		C(27)−Pd−Cl	96.3(5)
		N(2)−Pd−Cl	104.8(3)
		C(3)−N(2)−N(1)	115.1(11)
		N(1)−N(2)−Pd	133.0(9)
		N(2)−C(3)−C(19)	125.8(13)
		N(5)−C(4)−C(3)	115.7(13)
		C(4)−N(5)−Pd	118.6(10)

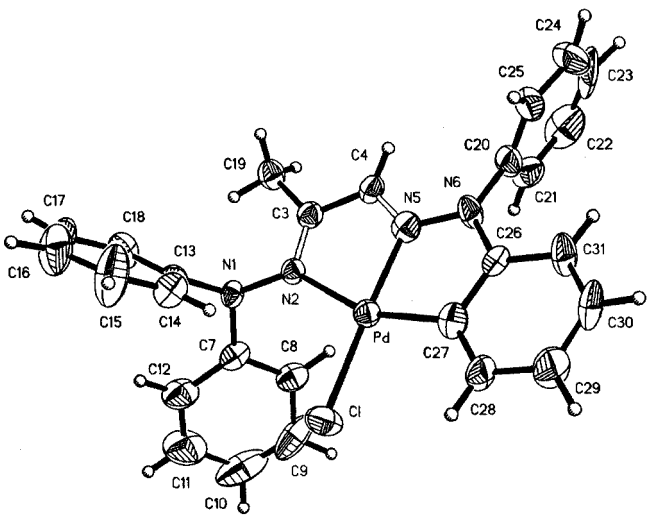
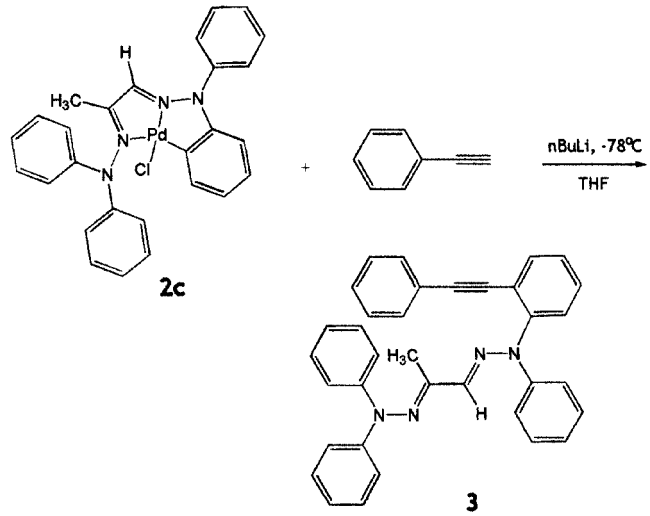


Fig. 1 Molecular Structure for Complex **2c**

ported analogous 112° [7]. The Pd-C bond distance 1.95(2) Å is shorter than those found in similar square planar palladium complexes [6,9,10,18] which could be associated with the overlapping of π electron cloud of aromatic ring to the *d* metal orbitals as suggested elsewhere [7].

Furthermore the reaction of **2c** in the presence of phenylacetylene and BuLi, afforded an organic compound **3** as a result of depalladation of complex **2c**, as shown in Scheme 2. IR spectrum of compound **3** shows a band at 2219 cm^{-1} which can be assigned to ν(C≡C). The ^{1}H and ^{13}C NMR spectra show additional signals corresponding to the phenylacetylene fragment, which is the result of transmetallation and reductive elimination process [1,2].



Scheme 2

Conclusions

Some new cyclopalladated complexes were synthesised containing N-donor imine ligands. The X-ray structure of **2c** reveals the distorted square planar coordination around the palladium atom. Complex **2c** was depalladated after the insertion of PhC≡C$^-$ nucleophile. Other similar reactions and their application in organic synthesis are still in progress.

Experimental Section

All reagents were obtained from commercial suppliers and used as received. Starting hydrazones were prepared by the corresponding ketones and N,N-diphenylhydrazine in ethanol according to reported procedures [20]. Infrared spectra were obtained with a Nicolet Magna 750 instrument. Melting points were measured on a Metl-b Temp II and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol Eclipse +300, chemical shifts (ppm) are relative to the TMS. The mass spectra were obtained on Jeol JMS-AX505 HA; The X-Ray Crystallography study for **2c** was done on a Siemens P4/PC diffractometer $\lambda_{(Mo\text{-}K\alpha)}$ = 0.71073 Å, graphite monochromator, T= 293 K, ω-2θ scan, range 1.5 < θ < 25°. Corrections were done for Lorentz and polarization effects. The structures were solved by direct methods; all nonhydrogen atoms were refined anisotropically by full least squares, (SHELXL-97) [21]. Absorption correction based on psi-scans was applied; hydrogen atoms bound to carbon atoms inserted at calculated position with isotropic temperature factor 1.2 times the U_{iso} of the parent carbon atom.

Bis(N,N′ diphenylhydrazone) of glyoxal **(1a)**

Compound **1a** was prepared from 0.3 mL (2.6 mmol) of glyoxal (40 % wt) and 1.14 g (5.2 mmol) of diphenylhydrazine. The product was obtained as a white solid 60 % yield, m.p. 207 °C.

IR ($CHCl_3$)ν_{max}: 1590 (C=N), 1494 (C=C) cm^{-1}; MS (EI): *m/z* = 390 [M^+, (100)], 316(19), 270(10), 222 [M^+-N(C_6H_5)$_2$, (10)], 168 [M^+-($C_{14}H_{11}N_3$), (32)], 77(5), 45(12), 29(5), 4(8); ^{1}H NMR (300 MHz, $CDCl_3$): 7.08 (8H, dd, J=7.68, 1.65 Hz, H-*o*), 7.13(2H, s, HC=N), 7.15 (4H, t, J=7.68 Hz, H-*p*), 7.36 (8H, td, J=7.68, 1.65 Hz, H-*m*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$):122.5 (C-*o*), 124.7 (C-*p*), 129.8 (C-*m*), 136.4 (H*C*=N), 143.4 (C-*i*) ppm.

***Bis-N,N-diphenylhydrazone of 2,3-Butanedione* (1b)**

Compound **1b** was prepared from 0.21 mL (2.4 mmol) of 2,3-Butanedione and 1.05 g (4.8 mmol) of diphenylhydrazine. The product was obtained as a yellow solid 50 % yield, m.p.190.5 °C.

IR ($CHCl_3$)ν_{max}: 1590 (C=N), 1488 (C=C) cm^{-1}; MS (EI): *m/z* = 418 [M^+, (100)], 390 [M^+-C_2H_4 (5)], 250 [M^+- N(C_6H_5)$_2$, (65)], 209(15), 182(10), 168 [M^+-($C_{16}H_{16}N_3$), (90)], 77(8), 4(9); ^{1}H NMR (300 MHz, $CDCl_3$):1.96 (6H, CH_3), 7.06-7.10 (12H, m, H-*o*, H-*p*), 7.31(8H, td, J=7.71, 1.35, Hz, H-*m*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$):16.6 (CH_3), 121.9 (C-*o*), 123.6 (C-*p*), 129.1 (C-*m*), 148.1 (C-*i*), 162.9 (CH_3C=N) ppm.

***Bis(N,N-diphenylhydrazone) of methylglyoxal* (1c)**

Compound **1c** was prepared from 0.35 mL (2.26 mmol) of methylglyoxal (40 % wt) and 1 g (4.5 mmol) of diphenylhydrazine. The product was obtained as a yellow solid 80 % yield, m.p.186.5 °C.

IR ($CHCl_3$)ν_{max}: 1590 (C=N), 1490 (C=C aromatic); MS (EI): *m/z* = 404 [M^+, (100)], 236 (M^+-N(C_6H_5)$_2$, (12)), 221(10), 168 [M^+- ($C_{15}H_{14}N_3$), (68)], 77(8); ^{1}H NMR (300 MHz, $CDCl_3$):1.99 (3H, s, CH_3), 7.02-7.07 (6H, m, H-*o*, H-*p*), 7.11-7.19 (7H, m, H-*o′*, H-*p′*, *H*C=N), 7.28 (4H, td, J=7.70, 1.65 Hz, H-*m*), 7.40(4H, td, J=7.70, 1.65 Hz, H-*m′*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$):15.6 (CH_3), 121.9 (C-*o*), 122.4(C-*o′*), 123.4 (C-*p*), 125.1 (C-*p′*), 129.1 (C-*m*), 130.0 (C-*m′*), 136.6 (H*C*=N), 143.1 (C-*i*), 148.2 (C-*i′*), 163.5 (CH_3C=N) ppm.

***1-Diphenylamino-10-chloro-5-phenyl-1,3,2-diazapalladolo[1,2-b]-1,2,3-benzodiazapalladol* (2a)**

Compound **2a** was prepared from 0.15 g (0.385 mmol) of Bis(*N,N*-diphenylhydrazone) of glyoxal (**1a**) and 0.136 g (0.77 mmol) of $PdCl_2$. the reaction mixture was stirred for 3 days at room temperature. The solid obtained was chromatographed on alumina using Hexane/CH_2Cl_2 as eluent. The product was obtained as a purple solid 95 % yield, m.p. 202 °C_{dec}.

IR ($CHCl_3$)ν_{max}: 1593 (C=N), 1488 (C=C aromatic) cm^{-1}; MS (FAB^+): *m/z* = 530 [M^+, (1)) 495[M^+-Cl, (3)], 307(35), 107(15), 77(10) 65(5); ^{1}H NMR (300 MHz, $CDCl_3$):5.79(1H, dd J=7.16 Hz, H-*3*), 6.63(1H, t, J=7.14, H-*4*), 6.77 (1H, t, J=7.14 Hz, H-*5*), 7.16-7.63(18H, m, H-*6*, H-*o*, H-*m*, H-*p*, H-*o′*, H-*m′*, H-*p′*, *H*C=N) ppm; ^{13}C NMR (75 MHz, $CDCl_3$):110.5 (C-*3*), 125.3 (C-*p′*), 125.5 (C-*5*), 126.6 (H*C*=N), 129.0 (C-*m*, C-*m′*), 129.7 (C-*o*, C-*p*), 130.6 (C-*1*), 131.2 (C-*6*), 143.0 (C-*2*) ppm.

***1-Diphenylamino-10-chloro-5-phenyl-2,3-dimethyl-1,3,2-diazapalladolo[1,2-b], 1,2,3-benzodiazapalladol* (2b)**

The title compound was prepared following the procedure described for **2a** from 0.17 g (0.4 mmol) of Bis(*N,N*-diphenylhydrazone) of 2,3-Butanedione (**1b**) and 0.15 g (0.8 mmol) of $PdCl_2$. The product was obtained as a purple solid (90 %), m.p. 256 °C.

IR ($CHCl_3$)ν_{max}: 1595 (C=N), 1488(C=C aromatic) cm^{-1}; MS (FAB^+): *m/z* = 523 [M^+-Cl, (2)). 307(37), 243(5), 167(4), 107(15), 77(11), 65(4);^{1}H NMR (300 MHz, $CDCl_3$):1.65 (3H, s, CH_3), 2.01 (3H, s, CH_3), 6.11 (1H, dd, J=7.68, 1.65 Hz, H-*3*), 6.67 (1H, td, J=7.68, 1.65 Hz, H-*4*), 6.75 (1H, td, J=7.68, 1.65 Hz, H-*5*), 7.18 (2H, t, J=7.14 Hz, H-*p′*), 7.26 (4H, d, H-*o′*), 7.40 (6H, t, J=7.68 Hz, H-*m*, H-*m′*), 7.46 (1H, dd, J=7.68, 1.65 Hz, H-*6*), 7.48-7.52 (3H, m, H-*o*, H-*p*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$):18.8 (CH_3), 112.6 (C-*3*), 148.9 (C-*o′*), 122.7 (C-*4*), 125.0 (C-*p′*), 125.5 (C-*5*), 128.1 (C-*m*), 129.5 (C-*m′*), 130.3 (C-*o*, C-*p*), 136.1 (C-*1*), 146.0 (C-*6*), 148.9 (C-*2*), 159.1 (C-*i*, C-*i′*), 174.4 (CH_3C=N) ppm

***1,6-diphenylamino-10-chloro-5-phenyl-2-methyl-1,3,2-diazapaladollo[1,2-b], 1,2,3-benzodiazapalladol* (2c)**

The title compound was prepared following the procedure described for **2a** from 0.125 g (0.309 mmol) Bis(*N,N*-diphenylhydrazone) of methylglyoxal (**1c**) and 0.109 g (0.618 mmol). The product was obtained as a purple solid 65 % yield, m.p. 190.5 °C.

IR ($CHCl_3$)ν_{max}: 1592 (C=N), 1487 (C=C aromatic) cm^{-1}; MS (FAB^+): *m/z* = 544 [M^+,(0.5)], 509 [M^+-Cl, (2)], 307(35), 107(15), 77(10), 65(5); ^{1}H RMN (300 MHz, $CDCl_3$): 1.90 (3H, s, CH_3), 5.81 (1H, dd, J=7.71, 1.65 Hz, H-*3*), 6.34(1H, s, HC=N), 6.68(1H, td, J=7.71, 1.65, Hz, H-*4*), 6.75 (1H, td, J=7.71, 1.65 Hz, H-*5*), 7.15 (2H, t, J=7.14 Hz, H-*p′*), 7.24 (4H, d, J= 7.14 Hz, H-o′), 7.33-7.38 (6H, m, H-*m′*), 7.46 (1H, dd, J=7.71, 1.65 Hz, H-*6*), 7.60-7.66 (3H, m, H-*o*, H-*p*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): 18.8 (CH_3), 111.3 (C-*3*), 146.1 (C-*o*), 122.8 (C-*4*), 125.0 (C-*p*), 125.5 (C-*5*), 128.1 (C-*p′*), 129.5 (C-*m*), 130.3 (C-*o′*, C-*p′*), 136.1 (C-*1*), 136.2 (C-*6*), 148.9 (C-*2*), 159.1 (C-*i′*, C-*i*), 172.2 (CH_3C=N) ppm.

***[N-phenyl-N-phenyl(2-phenylethenyl)-N′,N′-diphenyl hydrazone] of methylglyoxal* (3)**

To a solution of 0.3 g (0.55 mmol) of **2c** in diethylether, was added a solution consisting of 0.6 mL (0.55 mmol) phenylacetylene in diethylether and 0.3 mL of BuLi 1.6M at −78 °C. The reaction mixture was allowed to warm to room temperature and after 4 h of stirring the solvent was evaporated obtaining a black oil which was chromatographed on alumina using Hexane/AcOEt as eluent. The product was obtained as a yellow solid 20 % yield, m.p. 40 °C.

MS (FAB^+): *m/z* = 504 [M^+,(11)], 404 (5), 336(20), 309(10), 295(4), 309(9), 279(22), 267(15), 167(65), 149(100), 184(15), 71(30), 57(62), 43(56), 29(23), 18(5); ^{1}H RMN (300 MHz, $CDCl_3$): 1.99 (3H, s, CH_3), 6.99-7.24 (25H, m, *H*C=N, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): 15.6 (CH_3), 85.6 (C≡C), 95.1 (C≡C), 115.4, 121.1, 122.7. 123.2, 123.9, 128.2, 128.5, 128.7, 128.4, 128.9, 129.0, 130.3, 130.4, 131.5, 134.1, 136.6 (H*C*=N), 140.6 146.0, 148.1(C-*i*), 163.5.(CH_3C=N).

Supplementary material

The crystallography data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 185834 for compound **2c** Copies of this information may be obtained free of charge from to The director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: int.code+(1223)336-033;e-mail for inquiry: fileserv@ccdc.cam.ac.uk.

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