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Journal of Molecular Catalysis A: Chemical 241 (2005) 88–92
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Novel *N*-heterocyclic-carbene–rhodium complexes as hydrosilylation catalysts

Murat Yiğit [a], Ismail Özdemir [a,*], Bekir Çetinkaya [b], Engin Çetinkaya [b]

[a] *Inönü University, Faculty of Science and Art, Department of Chemistry, 44280 Malatya, Turkey*
[b] *Ege University, Faculty of Science, Department of Chemistry, 35100 Bornova-İzmir, Turkey*

Received 30 May 2005; received in revised form 4 July 2005; accepted 4 July 2005
Available online 15 August 2005

Abstract

Novel rhodium–1,3-dialkylperhydrobenzimidazolin-2-ylidene (**2a**,**b**) and 1,3-dialkylimidazolin-2-ylidene complexes (**4a**,**b**) have been prepared and characterized by C, H, N analysis, ^{1}H NMR and ^{13}C NMR. Triethylsilane reacts with acetophenone derivatives in the presence of catalytic amount of the new rhodium(I)–carbene complexes, RhCl(COD)(1,3-dialkylperhydrobenzimidazolin-2-ylidene) or RhCl(COD)(1,3-dialkylimidazolin-2-ylidene) to give the corresponding silylethers in good yields (63–99%).

Keywords: Perhydrobenzimidazolin-2-ylidene; Imidazolin-2-ylidene *N*-heterocyclic carbene; Hydrosilylation; Rhodium

1. Introduction

The number of synthetic applications of homogeneous catalysts has increased enormously during the last three decades. Highly active and selective catalysts have been prepared to activate a large variety of bonds, thus providing efficient methods to obtain new products with important industrial and pharmaceutical applications. However, homogeneous catalysts are far from being widely used in industrial processes, mainly due to their low chemical and thermal stability and to their low potential to provide recyclable systems. With this is in mind, recent research in this area has focused mainly on the search for new methods for the synthesis of stable, effective and recyclable catalysts, since this would combine both economic and environmental benefits.

Homogeneous organometallic catalysis has long depended on phosphane ligands [1,2]. Despite their effectiveness in controlling reactivity and selectivity, phosphane catalysts require air-free handling to prevent the oxidation of the ligand and have been subject to P–C activation at elevated temperatures. Recently, nucleophilic *N*-heterocyclic carbenes (NHCs) [3], with a stronger σ-donor electronic property than bulky tertiary phosphines [4], have emerged as a new family of ligands. In contrast to metal complexes of phosphines, the metal–NHC complexes appeared to be extraordinarily stable towards heat, air and moisture due to their high dissociation energies of the metal–carbon bond [5]. The precursor imidazolium salts are often easier to obtain than phosphines but preparation of the metal compounds from these salts can be more difficult [6]. The most common method is direct complexation of the free NHC, either isolated [7] or generated in situ [8] formed by deprotonation of the imidazolium salts. These methods require that the free NHC be stable and may be fatally complicated by the presence of other acidic protons in the ligand precursor. Oxidative addition of an imidazolinium carbon–hydrogen bond [9] to a low valent metal center and addition of an electron-rich olefin with C=C bond cleavage [10] can also lead to metal–NHC complexes in certain cases.

We have previously reported the use of a in situ formed imidazolidin-2-ylidenepalladium(II) system which exhibits high activity in various coupling reactions of aryl bromides and aryl chlorides [11]. In order to obtain a more stable, efficient and active system, we have also investigated benzo-annelated derivatives [12]. Recently, our group

* Corresponding author. Tel.: +90 42 2341 0212; fax: +90 42 2341 0212.
E-mail address: iozdemir@inonu.edu.tr (I. Özdemir).

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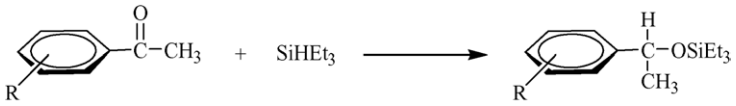
doi:10.1016/j.molcata.2005.07.012



Scheme 1.

reported that novel complexes of rhodium(I) based on 1,3-dialkyimidazolidin-2-ylidenes give good yields for the addition of phenylboronic acid to aldehydes [13].

The hydrosilylation is an important industrial process which inter alia is used for the synthesis of polysiloxanes and polysilanes [14]. Moreover, it is applied to the reduction of ketones to secondary alcohols [15]. In general, the term hydrosilylation is used to describe an addition reaction of hydrosilanes to double and triple bonds and in the laboratory, hydrosilylation is a very convenient method for the synthesis of a range of organosilicon compounds. The development of various hydrosilylation catalysts has already been summarized [16].

Although, rhodium–carbene complexes have been extensively studied, there are few reports on the hydrosilylation reactions of rhodium–carbene complexes in rhodium-mediated processes [17].

Based on these findings and our continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of rhodium–1,3-dialkylperhydrobenzimidazolin-2-ylidene and 1,3-dialkylimidazolin-2-ylidene complexes for the hydrosilylation of acetophenones. (Scheme 1).

We now report: (i) the straightforward preparation of new RhCl(COD)(1,3-dialkylperhydrobenzimidazolin-2-ylidene) and RhCl(COD)(1,3-dialkylimidazolin-2-ylidene) complexes and (ii) their efficient catalysis of the hydrosilylation of acetophenones.

2. Experimental

All reactions for the preparation of **1**–**4** were carried out under Ar in flame-dried glass-ware using standard Schlenk-type flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). Flash chromatography: Merck silica gel 60 (230–400 mesh). The complex $[RhCl(COD)]_2$ [18] and **1** and **3** were prepared according to known methods [19]. All reagents were purchased from Aldrich Chemical Co. All ^1H and ^{13}C NMR were performed in $CDCl_3$. ^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by Turkish Resarch Council (Ankara, Turkey) Microlab.

2.1. General procedure for the preparation of the rhodium–carbene complexes (**2a–b**, **4a–b**)

A solution of 1,3-dialkyl-perhydrobenzimidazolinylidene (**1**) or 1,3-dialkyl-4-methylimida-zolinylidene (**3**) (0.45 mmol) and $[RhClCOD]_2$ (0.45 mmol) in toluene (15 ml) was heated under reflux for 2 h. Upon cooling to room temperature, yellow-orange crystals of **2a**–**b**, **4a**–**b** were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 ml) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2/Et_2O.

2.2. Chloro(η^4-1,5-cyclooctadiene){1,3-bis(2,4,6-trimethylbenzyl)perhydrobenzimidazolin-2-ylidene}rhodium(I) , (**2a**)

^1H NMR (δ, $CDCl_3$): 0.74, 1.19 and 2.72 [m, 10H, NC*H*(CH_2)$_4$C*H*N]; 6.76 [s, 4H, $CH_2C_6H_2Me_3$-2,4,6]; 4.80, 6.21 and 5.21, 5.68 [d, 4H, J = 14.4 Hz and J = 14.6 Hz, $CH_2C_6H_2Me_3$-2,4,6]; 2.20 and 2.35 [s, 18H, $CH_2C_6H_2Me_3$-2,4,6]; 3.66 and 4.98 [m, 4H, CH_{COD}]; 1.90 and 2.33 [m, 8H, CH_{2COD}]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 230.01 [d, J = 47.2 Hz, $C_{carbene}$]; 24.70, 24.90, 28.70, 29.22, 50.59 and 51.05 [NCH(CH_2)$_4$CHN]; 129.64, 130.24, 130.29, 137.78, 137.82 and 138.60 [$CH_2C_6H_2Me_3$-2,4,6]; 69.54 and 70.04 [$CH_2C_6H_2Me_3$-2,4,6]; 21.27 and 21.37 [$CH_2C_6H_2Me_3$-2,4,6]; 68.85 and 99.36 [d, J = 14.7 Hz and J = 4.6 Hz CH_{COD}]; 29.69, 29.85,33.03 and 33.39 [CH_{2COD}]. Yield 0.22 g (80%), mp 236–238 °C, $\nu_{(NCN)}$ = 1425 cm^{-1}. Anal. cal. for $C_{34}H_{49}N_2ClRh$; C: 66.19, H: 7.56, N: 4.41; found C: 66.11, H: 7.40, N: 4.35.

2.3. Chloro(η^4-1,5-cyclooctadiene){1,3-bis(4-dimethylaminobenzyl)perhydrobenzimidazolin-2-ylidene}rhodium(I), (**2b**)

^1H NMR (δ, $CDCl_3$): 0.95, 1.55 and 2.87 [m, 10H, NC*H*(CH_2)$_4$C*H*N]; 6.21 and 7.35 [d, 8H, J = 8.8 Hz and J = 9.2 Hz, $CH_2C_6H_4NMe_2$-*p*]; 4.90, 5.92 and 5.02, 5.80 [d, 4H, J = 14.8 Hz and J = 15.2 Hz, $CH_2C_6H_4NMe_2$-*p*]; 2.92 and 2.94 [s, 12H, $CH_2C_6H_4NMe_2$-*p*]; 3.84 and 4.98 [m, 4H, CH_{COD}]; 1.86 and 2.70 [m, 8H, CH_{2COD}]; $^{13}C\{H\}$ NMR (δ, $CDCl_3$): 218.70 [d, J = 47.3 Hz, $C_{carbene}$]; 24.21, 24.44, 28.81, 28.84, 53.53 and 54.12 [NCH(CH_2)$_4$CHN]; 112.76, 125.55, 125.79, 128.91, 129.14, 150.12 and 150.28 [$CH_2C_6H_4NMe_2$-*p*]; 67.82 and 68.53 [$CH_2C_6H_4NMe_2$-*p*];

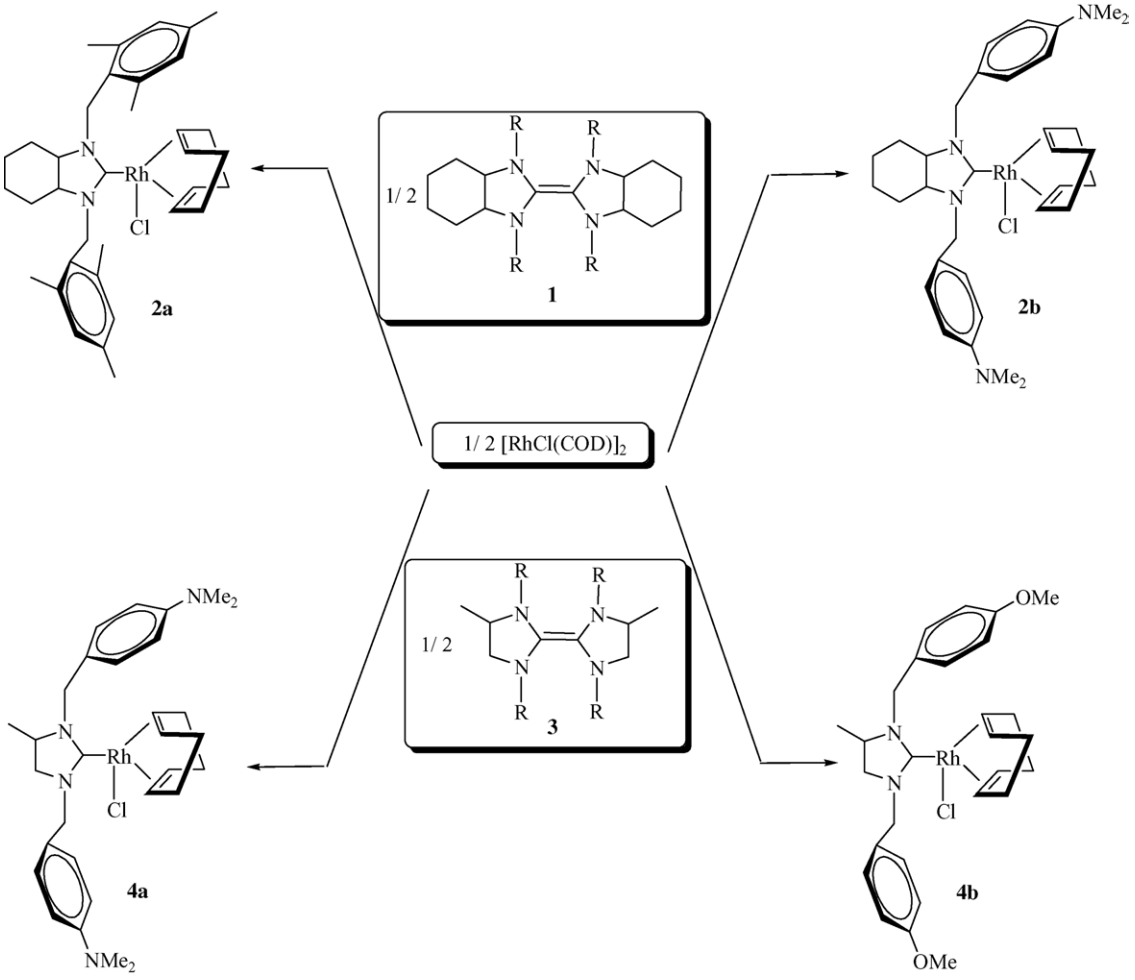
40.88 and 40.90 [$CH_2C_6H_4NMe_2$-*p*]; 69.15 and 99.38 [d, J = 14.5 Hz and J = 6.8 Hz CH_{COD}]; 29.32, 29.56, 32.96 and 33.04 [CH_{2COD}]. Yield 0.23 g (83%), mp 261 °C, $\nu_{(NCN)}$ = 1529 cm^{-1}. Anal. cal. for $C_{33}H_{46}N_4ClRh$; C: 59.68, H: 6.93, N: 8.44; found C: 59.58, H: 6.80, N: 8.53.

2.4. Chloro(η^4-1,5-cyclooctadiene){1,3-bis(4-dimethylaminobenzyl)-4-methylimidazolin-2-ylidene}rhodium(I),(4**a**)

^{1}H NMR (δ, $CDCl_3$): 3.44 [m, 1H, NC*H*(CH_3)CH_2N]; 2.81 and 3.32 [t, 2H, J = 10 Hz, NCH(CH_3)C*H*$_2$N]; 1.20 [d, 3H, J = 6.8 Hz, NCH(C*H*$_3$)CH_2N]; 6.73, 6.90 and 7.27, 7.45 [d, 8H, J = 8 Hz and J = 8.8 Hz, $CH_2C_6H_4NMe_2$-*p*]; 4.38, 6.29 and 5.15, 5.84 [d, 4H, J = 14 Hz and J = 14.4 Hz, C*H*$_2C_6H_4NMe_2$-*p*]; 2.92 and 2.94 [s, 12H, $CH_2C_6H_4NMe_2$-*p*]; 3.50 and 5.01 [m, 4H, C*H*$_{COD}$]; 1.93 and 2.33 [m, 8H, C*H*$_{2COD}$]; ^{13}C{H} NMR (δ, $CDCl_3$): 211.02 [d, J = 46.6 Hz, $C_{carbene}$]; 19.04, 53.45 and 55.43 [NCH(*C*H$_3$)*C*H$_2$N]; 112.90, 123.78, 124.44, 124.55, 128.82, 129.43, 130.06, 150.26 and 150.51 [$CH_2C_6H_4NMe_2$-*p*]; 54.41 and 54.68 [*C*H$_2C_6H_4NMe_2$-*p*]; 40.81 and 40.83 [$CH_2C_6H_4NMe_2$-*p*]; 68.40 and 99.23 [d, J = 13.0 Hz and J = 6.9 Hz *C*H$_{COD}$]; 28.81, 28.99, 32.98 and 33.16 [*C*H$_{2COD}$]. Yield 0.22 g (82%), mp 115 °C, $\nu_{(NCN)}$ = 1523 cm^{-1}. Anal. cal. for $C_{30}H_{42}N_4ClRh$; C: 60.35, H: 7.09, N: 9.38; found C: 60.45, H: 7.20, N: 9.43.

2.5. Chloro(η^4-1,5-cyclooctadiene){1,3-bis(4-methoxybenzyl)-4-methyl imidazolin-2-ylidene} rhodium(I), (**4b**)

^{1}H NMR (δ, $CDCl_3$): 3.42 [m, 1H, NC*H*(CH_3)CH_2N]; 2.82 and 3.33 [t, 2H, J = 10 Hz, NCH(CH_3)C*H*$_2$N]; 1.03 [d, 3H, J = 6.4 Hz, NCH(C*H*$_3$)CH_2N]; 6.87, 6.91 and 7.35, 7.52 [d, 8H, J = 8.0 Hz and J = 8.4 Hz, $CH_2C_6H_4$OMe-*p*]; 4.42, 5.34 and 5.25, 6.32 [d, 4H, J = 14.8 Hz and J = 14.4 Hz, C*H*$_2C_6H_4$OMe-*p*]; 3.78 and 3.80 [s, 6H, $CH_2C_6H_4$O*Me*-*p*]; 3.53 and 5.03 [m, 4H, C*H*$_{COD}$]; 1.96 and 2.43 [m, 8H, C*H*$_{2COD}$]; ^{13}C{H} NMR (δ, $CDCl_3$): 212,47 [d, J = 46.4 Hz, $C_{carbene}$]; 19.18, 53.72 and 55.65 [NCH(*C*H$_3$)*C*H$_2$N]; 114.44, 114.56, 128.19, 128.87, 129.14,



Scheme 2. Synthesis of rhodium–carbene complexes (**2a**,**b** and **4a**,**b**).

129.87, 130.01, 130.54, 159.46 and 159.67 [$CH_2C_6H_4OMe$-*p*]; 54.72 and 54.86 [$CH_2C_6H_4OMe$-*p*]; 51.54 and 51.65 [$CH_2C_6H_4OMe$-*p*]; 69.25 and 99.70 [d, $J = 14.5$ Hz and $J = 6.1$ Hz CH_{COD}]; 28.94, 29.12, 30.01 and 33.91 [CH_{2COD}]. Yield 0.22 g (86%), mp 181 °C, $\nu_{(NCN)} = 1510\ cm^{-1}$. Anal. cal. for $C_{28}H_{36}N_2O_2ClRh$; C: 58.90, H: 6.36, N: 4.91; found C: 58.81, H: 6.34, N: 4.83.

2.6. General procedure for rhodium–carbene catalyzed addition of acetophenone to triethylsilane

Acetophenone (1 mmol), triethylsilane (1.25 mmol) and rhodium carbene catalyst (0.5 mol % based on ketone) were introduced in to schlenk tube. The resulting mixture was heated for 2 h at 90 °C, cooled to ambient temperature, purified by flash chromatography (hexane/ethyl acetate, 10/1). Analysis of the reaction product was carried out by NMR spectroscopy and GC.

3. Results and discussion

3.1. Synthesis and characterisation of RhCl(COD)NHC

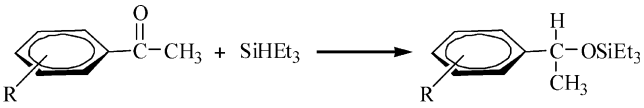
The bis(1,3-dialkylperhydrobenzimidazolin-2-ylidene) (**1**) and bis(1,3-dialkylimidazolin-2-ylidene) (**3**), were synthesised using a method similar to that reported by Lappert and co-workers [19]. The reaction of bis(1,3-dialkylperhydrobenzimidazolin-2-ylidene) (**1**) or bis(1,3-dialkylimidazolin-2-ylidene) (**3**), with the binuclear $[RhCl(COD)]_2$ complex proceeded smoothly in refluxing toluene to give the RhCl(COD)(1,3-dialkylperhydrobenzimidazolin-2-ylidene) (**2a**,**b**) or RhCl(COD)(1,3-dialkylimidazolin-2-ylidene) complexes (**4a**,**b**) as crystalline solids in 80–86% yields (Scheme 2). Each rhodium compound was fully characterized by ^1H and ^{13}C NMR spectroscopy, FT-IR and elemental analysis.

The rhodium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1425–1529 cm^{-1} [20]. ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the range 211.02–230.01 ppm and are similar to those found in other carbene complexes. Coupling constants $J(^{103}Rh–^{13}C)$ for the new rhodium complexes (**2** and **4**) are comparable with those found for carbene rhodium(I) complexes. These new complexes show typical spectroscopic signatures which are in line with those recently reported for RhCl(COD)(1,3-dialkylimidazolin-2-ylidine) complexes [20].

3.2. Hydrosilylation of acetophenone derivatives

Hydrosilylation reactions involve the addition of inorganic or organic silicon hydrides to multiple bonds such as alkyne, alkene, ketoxime and carbonyl groups. Metal complexes are able to catalyze hydrosilylation reaction of organic substrate under mild conditions and are very attractive for many processes. We have observed that Rh(I) complexes of 1,3-dialkylperhydrobenzimidazolin-2-ylidene and 1,3-dialkylimidazolin-2-ylidene can be used as effective catalysts for the hydrosilylation of acetophenone derivatives. Rhodium–NHC complexes (**2** and **4**) are found to be active catalysts for the hydrosilylation of acetophenone derivatives and the addition of triethylsiliane to acetophenone proceeds in high yields and quite rapidly even with a low catalyst loading. *N*-heterocyclic carbene complexes used herein showed higher catalytic efficiency and higher conversion time towards the hydrosilylation of aceophenone derivatives than the corresponding carbene complexes [17a]. All reaction were carried out without any special need for inert conditions, since the catalysts used proved to be fairly stable under oxygen-containing atmospheres, even at high temperatures. The results are summarized in Table 1. Under those conditions, acetophenone, 2-methoxyacetophenone, 3-methoxyacetophenone and 4-chloroacetophenone react very cleanly with triethylsilane in goods yields (Table 1, entries 2, 8, 12 and 14). These results are in agreement with other reports on rhodium–carbene catalyzed hydrosilylation of carbonyl compounds [17a,f].

Table 1
Hydrosilylation of acetophenone derivatives



Entry	R	Catalyst	Yield[a,b,c] (%)
1	H	**2a**	93
2	H	**2b**	95
3	H	**4a**	90
4	H	**4b**	91
5	*o*-OMe	**2a**	92
6	*o*-OMe	**2b**	98
7	*o*-OMe	**4a**	96
8	*o*-OMe	**4b**	99
9	*m*-OMe	**2a**	90
10	*m*-OMe	**2b**	98
11	*m*-OMe	**4a**	98
12	*m*-OMe	**4b**	99
13	*p*-Cl	**2a**	63
14	*p*-Cl	**2b**	73
15	*p*-Cl	**4a**	68
16	*p*-Cl	**4b**	71

[a] *Reaction conditions*: 1.0 mmol of acetophenone, 1.25 mmol of triethylsilane, 0.5 mmol% (based on ketone) **2** or **4**.
[b] Purity of compounds is checked by GC and yields are based on ketone.
[c] Temperature 90 °C, 2 h.

4. Conclusion

In summary, from readily available starting materials, such as bis(1,3-dialkylperhydrobenzimidazolin-2-

ylidene) and bis(1,3-dialkylimidazolin-2-ylidene) four novel rhodium–carbenes (**2a**,**b** and **4a**,**b**) have been prepared and characterized. Also, we have investigated the hydrosilylation activity of them for acetophenone derivatives resulting in the formation of the corresponding silylethers. The future work will explore the development of an asymmetric version of this process.

Acknowledgements

This work was financially supported by the Technological and Scientific Research Council of Turkey TÜBİTAK [TBAG-2474 (104T085)] and Inönü University Research Fund (BAP:2005/42).

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