Journal of Organometallic Chemistry, 466 (1994) 259-263

Iridium complexes of 2-(2′-thienyl)pyridine

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(Received June 1, 1993)

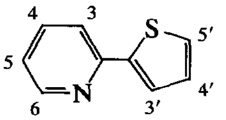
Abstract

2-(2′-Thienyl)pyridine (Hthpy) reacts with $[Ir(CO)(MeCN)(PPh_3)_2]PF_6$ (**1**) in dichloromethane at room temperature to give $[Ir(CO)(Hthpy)(PPh_3)_2]PF_6$ (**2**), which contains an *N*-bound Hthpy. Direct cyclometallation occurs when the chelating ligand reacts with **1** under reflux conditions in dichloromethane/2-methoxyethanol solution. The product $[Ir(H)(thpy)(CO)(PPh_3)_2]PF_6$ (**3**) can also be obtained through thermal rearrangement of **2**. The structures of **2** and **3** have been determined by single crystal X-ray diffraction studies.

Key words: Iridium; Pyridine; Thienyl; Cyclometallation

1. Introduction

Cyclometallation of thiophene derivatives is still a relatively unexplored field [1–3]. 2-(2′-Thienyl)pyridine (Hthpy) can afford σ-thienyl complexes through formation of *N*,*C*-chelates [4–7], but can also act as a simple monodentate *N*-donor [7,8] and occasionally as a bidentate *N*,*S*-donor [7].



We have recently investigated the activation of aromatic and aliphatic C–H bonds [9–11]. In particular, we found that 2-phenylpyridine (ppyH) readily coordinates via nitrogen to Ir^I and cyclometallates under more vigorous conditions [10]. Given the structural similarity of Hthpy and ppyH we studied the interaction of Ir^I with Hthpy. Here we describe the syntheses and structural characterization of two iridium complexes which contain monodentate *N*-bonded Hthpy and bidentate *N*,*C*-bonded thpy, respectively.

2. Results and discussion

2-(2′-Thienyl)pyridine (Hthpy) replaces acetonitrile in $[Ir(CO)(MeCN)(PPh_3)_2]PF_6$ (**1**) under very mild conditions. The product $[Ir(CO)(Hthpy)(PPh_3)_2]PF_6$ (**2**) is a bright yellow air-stable crystalline solid which behaves as a 1 : 1 electrolyte in dichloromethane. The IR spectrum of **2** shows a strong ν(CO) at 1991 cm^{-1}, higher than in **1** [12]. The single ^{31}P NMR spectrum of **2** is consistent with the two *trans* PPh_3 groups. The chemical shift (δ 25.5) is similar to that of related cationic Ir^I species [10].

The presence of an *N*-bound Hthpy is apparent from the ^1H and ^{13}C NMR spectra of **2**. The non-metallated thienyl ring gives rise to an AMX pattern in the ^1H NMR spectrum, where the signal corresponding to H-5′ is masked by PPh_3 phenyl resonances (see Experimental section). The ^{13}C NMR spectrum in CD_2Cl_2 reveals 13 signals, 8 of which can be assigned to the Hthpy. Two weak resonances (at δ 154.3 and δ 138.4) could be assigned to quaternary carbon atoms of Hthpy using the SFORD (single-frequency off-resonance decoupling) technique, and the missing resonance is probably obscured by one of the more intense PPh_3 carbon signals.

The crystal structure of **2** consists of discrete $[Ir(CO)(Hthpy)(PPh_3)_2]^+$ cations and $[PF_6]^-$ anions

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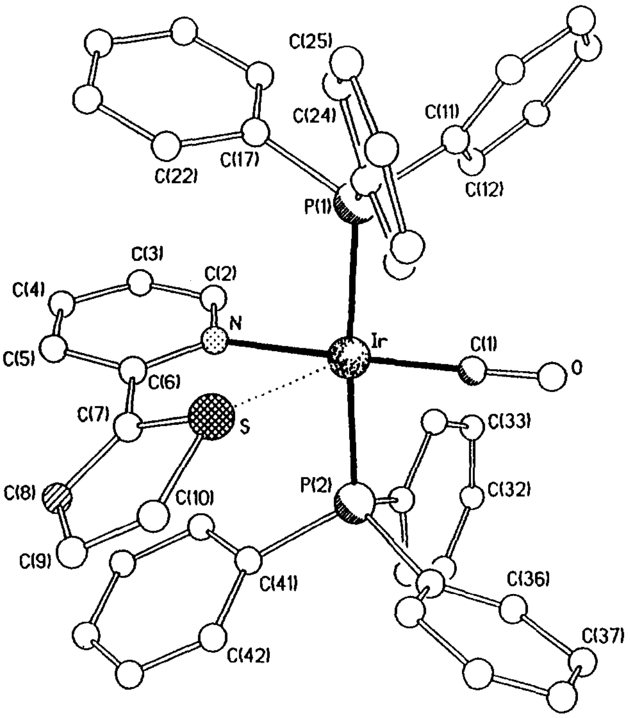

Fig. 1. View of the complex cation of [Ir(CO)(Hthpy)(PPh$_3$)$_2$]PF$_6$ (2) with the atomic numbering scheme.

with no interionic contacts. A drawing of the cation is shown in Fig. 1. Crystal data are listed in Table 1 and relevant bond parameters are reported in Table 2.

The coordination is distorted square-planar with the Ir atom removed by 0.09 Å from the mean plane through C(1), N, P(1), and P(2) atoms. The Ir–N distance of 2.117(8) Å is similar to those reported for Ir complexes containing monodentate aromatic *N*-donors [10,13]. The thienyl ring is twisted by 31.1° with respect to the pyridine moiety. This torsion allows the sulphur atom to occupy an axial position above the coordination plane. Although less than the sum of their van der Waals radii, the Ir–S distance of 3.045(4) Å is well outside the range (2.29–2.41 Å) reported for normal M–S(thiophene) bonds [14–17]. The present metal–sulphur separation approaches those observed for weak, long-range apical interactions in macrocyclic thioether complexes [18].

The reaction of Hthpy with **1** in dichloromethane/2-methoxyethanol (2:5, v/v) under reflux for 20 h affords a mixture of **2** (as the minor component) and a cyclometallated hydrido-species which was formulated as [Ir(H)(thpy)(CO)(PPh$_3$)$_2$]PF$_6$ (**3**). The same complex could be obtained in a slightly lower yield by thermal rearrangement of **2** under similar experimental conditions (24 h reflux in CH$_2$Cl$_2$/2-methoxyethanol). However, in the latter case a minor unidentified product was detected in the reaction mixture. It is apparent

TABLE 1. Crystal and refinement data for [Ir(CO)(Hthpy)(IPPh$_3$)$_2$]PF$_6$ (**2**) and [Ir(H)(thpy)(CO)(PPh$_3$)$_2$]PF$_6$ (**3**)

	2	**3**
Formula	$C_{46}H_{37}F_6IrNOP_3S$	$C_{46}H_{37}F_6IrNOP_3S$
FW	1050.9	1050.9
Space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
a, Å	19.752(7)	13.646(3)
b, A	19.433(5)	13.674(4)
c, Å	22.544(7)	23.344(6)
β, deg		105.29(2)
V, Å^3	8653(5)	4202(2)
Z	8	4
ρ_{calc}, g cm^{-3}	1.613	1.661
Cryst. size, mm	0.32×0.12×0.32	0.36×0.20×0.12
μ (Mo Kα), cm^{-1}	33.07	34.06
Range of transm factors	0.286–0.364	0.376–0.499
T, °C	22±2	22±2
λ, Å	0.71073	0.71073
Scan mode	ω	ω
2θ range, deg	3.0–50.0	3.0–50.0
Reflctns. measd.	$h, k, -l$	$h, k, \pm l$
No. of data	8383	8234
No. of unique data	7663	7415
No. of data obsd.	3949 [$I > 3\sigma(I)$]	5148 [$I > 3\sigma(I)$]
Params. refined	347	347
R [a]	0.047	0.046
R_w [b]	0.048	0.044
S [c]	1.22	1.77
q factor	0.001	0.0003

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$; $w^{-1} = \sigma(F_o)^2 + q(F_o)^2$. [c] goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

TABLE 2. Selected bond distances (Å) and angles (deg) for [Ir(CO)(Hthpy)(PPh$_3$)$_2$]PF$_6$ (**2**)

Bond distances			
Ir–P(1)	2.330(3)	Ir–P(2)	2.333(3)
Ir–C(1)	1.818(12)	Ir–N	2.117(8)
Ir···S	3.045(4)	C(1)–O	1.150(16)
N–C(2)	1.349(14)	S–C(7)	1.696(12)
N–C(6)	1.366(14)	C(2)–C(3)	1.357(17)
C(3)–C(4)	1.329(24)	C(4)–C(5)	1.400(19)
C(5)–C(6)	1.393(17)	C(6)–C(7)	1.455(15)
C(7)–C(8)	1.365(17)	C(8)–C(9)	1.414(25)
C(9)–C(10)	1.328(26)	S–C(10)	1.691(16)
Angles			
P(1)–Ir–P(2)	174.4(1)	P(1)–Ir–N	92.2(2)
P(2)–Ir–N	91.1(2)	P(1)–Ir–C(1)	88.1(4)
P(2)–Ir–C(1)	88.3(4)	N–Ir–C(1)	175.7(4)
Ir–N–C(2)	114.4(7)	Ir–N–C(6)	127.1(7)
C(2)–N–C(6)	118.5(9)	C(7)–S–C(10)	91.2(7)
Ir–C(1)–O	177.4(12)	N–C(2)–C(3)	123.5(12)
C(2)–C(3)–C(4)	119.6(13)	C(3)–C(4)–C(5)	119.0(12)
C(4)–C(5)–C(6)	120.5(12)	N–C(6)–C(5)	118.7(10)
N–C(6)–C(7)	120.4(9)	C(5)–C(6)–C(7)	120.9(10)
S–C(7)–C(6)	123.9(8)	S–C(7)–C(8)	112.8(9)
C(6)–C(7)–C(8)	123.2(11)	C(7)–C(8)–C(9)	109.7(13)
C(8)–C(9)–C(10)	114.2(14)	S–C(10)–C(9)	112.0(13)

that in both cases the metal adds oxidatively a C–H bond of Hthpy with preservation of the Ir–H fragment.

The IR spectrum of **3** shows a sharp ν(CO) at 2064 cm^{-1} and ν(Ir–H) at 2234 cm^{-1}. A triplet at δ −15.2 (^2J(PH) = 12.3 Hz) was observed in the ^{1}H NMR spectrum of **3**, thereby confirming the presence of a hydride *cis* to two PPh$_3$ groups. The chemical shift also suggests that the Ir–H group must be *trans* to an *N*-donor [9,19]. The presence of a metallated thienyl ring in **3** is apparent from the ^{1}H and ^{13}C NMR spectra. Thus, the proton AMX spin system observed for the non-metallated thienyl portion of Hthpy in complex **2** becomes an AX system upon metallation and two doublets are observed at δ 6.99 and δ 6.55 (^3J(HH) = 4.8 Hz). On the other hand, the metallated carbon resonance was observed as a triplet (^2J(PC) = 12.2 Hz) at δ 152.5, downfield from the free ^{13}C NMR signal [6].

The solid state structure of **3** has been determined by X-ray crystallography. Crystal data and relevant bond distances and angles are listed in Tables 1 and 3, respectively. A perspective view of the complex cation of **3** is shown in Fig. 2. Complex **3** is isostructural with [Ir(H)(bq)(CO)(PPh$_3$)$_2$]PF$_6$ (bq = 7,8-benzoquinolinate) [9], with the thpy bound through the N atom and an orthometallated thienyl carbon atom. The Ir–N distance of 2.198(6) Å is slightly longer than the corresponding distance in **2** due to the presence of a stronger *trans* director. The Ir–C distance (2.037(8) Å) is similar to the corresponding distance in Ir$^{\text{III}}$ *N*,*C*-chelates with similar geometry [9,20]. The thienyl and pyridine rings are almost coplanar (dihedral angle 3.7°) and the bite angle at the metal (77.5(3)°) appears to be smaller than that observed for [Pt(thpy)(Hthpy)I] [4] (N–Pt–C = 80.6(7)°), the only crystallographically characterized complex containing a cyclometallated thpy. Although the hydride was located in the final difference Fourier map, attempts to refine its position afforded unreasonably short Ir–H distances.

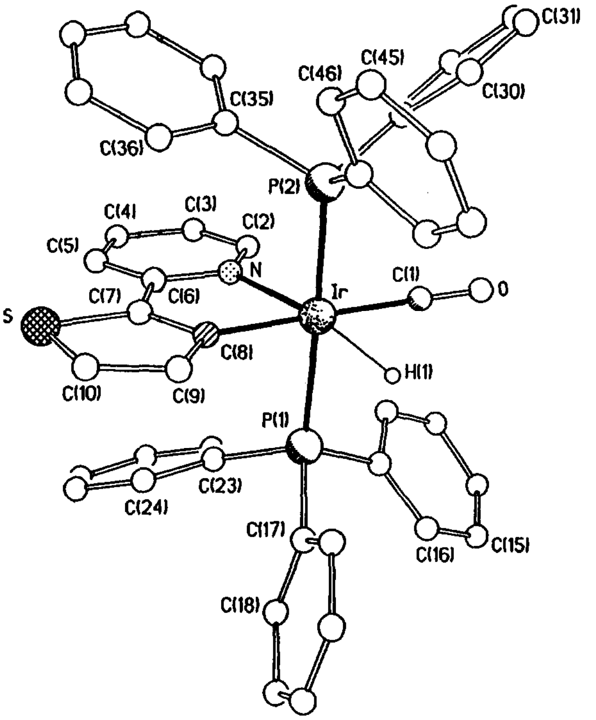

Fig. 2. Drawing of the cationic unit of [Ir(H)(thpy)(CO)(PPh$_3$)$_2$]PF$_6$ (**3**) showing the labelling scheme of the atoms.

TABLE 3. Selected bond distances (Å) and angles (deg) for [Ir(H)(CO)(thpy)(PPh$_3$)$_2$]PF$_6$ (**3**)

Bond distances			
Ir–H(1)	1.931	Ir–P(1)	2.359(2)
Ir–P(2)	2.353(2)	Ir–N	2.198(6)
Ir–C(1)	1.908(9)	Ir–C(8)	2.037(8)
N–C(2)	1.342(12)	N–C(6)	1.347(11)
C(1)–O	1.137(12)	C(2)–C(3)	1.355(14)
C(3)–C(4)	1.394(18)	C(4)–C(5)	1.350(19)
C(5)–C(6)	1.402(13)	C(6)–C(7)	1.434(13)
C(7)–C(8)	1.355(11)	C(8)–C(9)	1.431(13)
C(9)–C(10)	1.404(13)	S–C(7)	1.725(9)
S–C(10)	1.720(11)		
Angles			
P(1)–Ir–P(2)	174.4(1)	H(1)–Ir–P(1)	81.5
P(2)–Ir–N	91.8(2)	H(1)–Ir–P(2)	96.0
P(1)–Ir–N	90.4(2)	H(1)–Ir–C(1)	78.5
P(1)–Ir–C(1)	93.0(2)	H(1)–Ir–C(8)	98.4
P(2)–Ir–C(1)	91.4(2)	N–Ir–C(1)	105.9(3)
C(1)–Ir–C(8)	176.3(3)	P(1)–Ir–C(8)	88.4(2)
P(2)–Ir–C(8)	87.0(2)	N–Ir–C(8)	77.5(3)
Ir–C(8)–C(9)	134.5(6)	Ir–C(1)–O	175.1(8)
Ir–C(8)–C(7)	115.5(6)	Ir–N–C(6)	113.2(6)
Ir–N–C(2)	127.7(6)		

3. Experimental section

All reactions were carried out under dinitrogen in dried solvents. 2-(2'-Thienyl)pyridine (Lancaster) was used as received without further purification. [Ir(CO)(MeCN)(PPh$_3$)$_2$]PF$_6$ was prepared according to the literature [12].

The ^{1}H (300.13 MHz), ^{13}C (75.469 MHz) and ^{31}P (121.5 MHz) NMR spectra were run on a Bruker AC 300 spectrometer. Chemical shifts are referenced to internal TMS (^{1}H and ^{13}C) and to external 85% H$_3$PO$_4$ (^{31}P). IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer as Nujol mulls. Conductivity measurements were carried out using an LKB 5300 B Conductolyser conductivity bridge. Analyses were performed by the Microanalytical Laboratory of our department.

3.1. $[Ir(CO)(Hthpy)(PPh_3)_2]PF_6$ (2)

A colourless solution of 2-(2'-thienyl)pyridine (15 mg, 0.093 mmol) in CH_2Cl_2 (5 ml) was added to a yellow solution of $[Ir(CO)(MeCN)(PPh_3)_2]PF_6$ (75 mg, 0.081 mmol) in CH_2Cl_2 (2 ml). No colour change was observed. After 2 h stirring, slow addition of diethyl ether afforded **2** as yellow needles (70 mg, 83%). Anal. Found: C, 52.50; H, 3.54; N, 1.18. $C_{46}H_{37}F_6IrNOP_3S$ calcd.: C, 52.57; H, 3.55; N, 1.33%. IR: ν(CO) 1991s, ν(PF) 839s br cm^{-1}. Λ_M (10^{-4} M in CH_2Cl_2) 49.82 Ω^{-1} mol^{-1} cm^2. NMR: $^{31}P\{^1H\}$(CH_2Cl_2/Acetone-d_6(20%)) δ 25.5 (s, PPh_3), −143.1 (septet, J(PF) = 710 Hz, PF_6^-); ^1H (CD_2Cl_2) δ 7.95 (br d, $J \approx 6$ Hz, H-6), 7.52–7.28 (m, PPh_3 + H-5' + H-4), 7.24 (br d, $J \approx 8$ Hz, H-3), 7.09 (dd, $J = 3.8$, $J = 1.2$ Hz, H-3'), 6.99 (dd, $J = 5.0$, $J = 3.8$ Hz, H-4'), 6.52 (ddd, $J = 7.5$, $J = 5.9$, $J = 1.4$ Hz, H-5); $^{13}C\{^1H\}$ (CD_2Cl_2) δ 174.0 (t, J(PC) = 12 Hz, Ir–CO), [154.3, 151.8, 138.9, 138.4, 130.6, 128.9, 126.6, 123.9, 8 aromatic C, Hthpy], [134.3 (t, $J = 6.1$ Hz, *ortho* C), 131.8 (s, *para* C), 130.1 (t, $J = 27.5$ Hz, *ipso* C), 129.3 (t, $J = 5.3$ Hz, *meta* C), PPh_3].

3.2. $[Ir(H)(CO)(thpy)(PPh_3)_2]PF_6$ (3)

(a) 2-Methoxyethanol (15 ml) was added to a solution of $[Ir(CO)(MeCN)(PPh_3)_2]PF_6$ (200 mg, 0.215 mmol) and 2-(2'-thienyl)pyridine (44 mg, 0.273 mmol) in CH_2Cl_2 (6 ml). The resultant yellow-green solution was stirred under reflux for 20 h. A small amount of black metallic solid was separated by filtration and the filtrate was concentrated under reduced pressure. Addition of diethyl ether caused the formation of a pale yellow powder (130 mg), a mixture of the non-metallated complex **2**, and **3**, in the approximate ratio of 1:5. Recrystallization of this mixture from CH_2Cl_2-Et_2O afforded **3** as very pale yellow prisms. Anal. Found: C, 52.53; H, 3.51; N, 1.48. $C_{46}H_{37}F_6IrNOP_3S$ calcd.: C, 52.57; H, 3.55; N, 1.33%. IR: ν(IrH) 2234w, ν(CO) 2064s, ν(PF) 836s br cm^{-1}. Λ_M (10^{-4} M in CH_2Cl_2) 60.78 Ω^{-1} mol^{-1} cm^2. NMR: $^{31}P\{^1H\}$(CH_2Cl_2/Acetone-d_6(20%)) δ 7.8 (s, PPh_3), −142.8 (septet, J(PF) = 710 Hz, PF_6^-); ^1H (CD_2Cl_2) δ 8.52 (br d, $J = 5.3$ Hz, H-6), 7.52–7.25 (m, PPh_3 + H-4), 6.99 (d, $J = 4.8$ Hz, H-4' or H-5'), 6.87 (m, $J = 7.0$, $J = 5.3$, $J = 1.0$ Hz, H-5), 6.63 (br d, $J \approx 8$ Hz, H-3), 6.55 (d, $J = 4.8$ Hz, H-5' or H-4') −15.20 (t, ^2J(PH) = 12.3 Hz, Ir–H); $^{13}C\{^1H\}$ (CD_2Cl_2) δ 174.5 (t, J(PC) = 7.4 Hz, Ir–CO), [159.8, 152.6, 152.5 (t, J(PC) = 12.2 Hz, metallated C-3'), 145.8, 139.0, 138.8, 129.9, 122.4, 120.2, 9 aromatic C, Hthpy], [133.7 (t, $J = 5.7$ Hz, *ortho* C), 131.8 (s, *para* C), 129.1 (t, $J = 5.3$ Hz, *meta* C), 128.5 (t, $J = 29.6$ Hz, *ipso* C), PPh_3].

(b) A solution of **2** (50 mg, 0.048 mmol) in CH_2Cl_2 (3 ml) and 2-methoxyethanol (7 ml) was heated under reflux for 24 h. The pale yellow solution was then concentrated to *ca.* 1 ml. Addition of Et_2O led to the precipitation of a pale yellow solid (30 mg). Spectroscopic (IR and NMR) characterization of the product revealed the presence of a *ca.* 5:1 mixture of **3** with an unidentified species with a ν(CO) at 1952 cm^{-1}.

3.3. X-ray structure analysis

Crystals of **2** and **3** suitable for an X-ray diffraction study were obtained by diffusion of Et_2O into their saturated CH_2Cl_2 solutions. Diffraction data were collected on a Siemens R3m/V four-circle diffractometer with an ω-2θ scan method using graphite-monochromated Mo Kα radiation. All observed intensities for both compounds were corrected for absorption using an empirical method based on Ψ scans [21].

Both structures were solved by standard heavy-atom methods, which allowed the location of the Ir and P atoms, followed by difference Fourier syntheses and subsequent least-squares refinement. All calculations were performed with the Siemens SHELXTL PLUS [22] and PARST [23] programs. Atomic scattering factors and anomalous dispersion terms were those supplied in the Siemens structure determination package.

3.3.1. $[Ir(CO)(Hthpy)(PPh_3)_2]PF_6$ (2)

Cell constants, standard deviations, and the orientation matrix were obtained by least-squares treatment of the angular coordinates of 20 intense independent reflections in the range $14.8° \le 2\theta \le 29.8°$. The space group *Pbca* was uniquely identified on the basis of the systematic absences observed during the data collection. The Ir, P, N, S, C atoms of the Hthpy and the CO group atoms were included in the refinement with anisotropic thermal parameters. The hydrogen atoms were placed in a combination of observed and calculated positions, then held in idealized positions (d(C–H) = 0.96 Å) with a common isotropic temperature factor ($U = 0.05$ $Å^2$). The fluorine atoms of the PF_6^- anion were found disordered in two positions with group occupancies of 0.60 and 0.40, respectively.

3.3.2. $[Ir(H)(thpy)(CO)(PPh_3)_2]PF_6$ (3)

Unit cell dimensions were obtained by centring 25 reflections having 2θ values between 15.3° and 28.0°. The space group $P2_1/n$ was uniquely determined by the observed conditions: $h0l$, $h + l = 2n$; $0k0$, $k = 2n$. No decay in the intensities of two standard reflections occurred throughout the data collection.

All non-hydrogen atoms were assigned anisotropic displacement parameters except the phenyl carbons and the fluorine atoms of the $[PF_6]^-$. The latter were found disordered in two positions with occupancy factors calculated at 0.72 and 0.28, respectively. The hydride was located from difference Fourier map, but not refined. The remaining hydrogen atoms were added in their idealized position (d(C–H) = 0.96 Å) with their isotropic thermal parameters set at $U = 0.05$ Å^2. A complete list of bond distances and angles, anisotropic temperature factors, and hydrogen coordinates is available from the authors and from the Cambridge Crystallographic Data Centre.

Acknowledgment

We wish to thank the Italian Ministero per l'Università e la Ricerca Scientifica e Tecnologica (MURST) for financial support.

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