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Star-shaped polyferrocenes based on thiophene and triphenylamine: synthesis, spectroscopy and electrochemistry

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Abstract

Star-shaped tri- and tetra-ferrocenes anchored on triphenylamine or thiophene cores were obtained by palladium-catalyzed cross-coupling reactions in moderate to good yields. These polymetallic systems were characterized by NMR, UV–vis and mass spectral methods, elemental analyses and by electrochemical studies. As observed earlier for tris(ferrocenyl)benzenes, these complexes also lack electronic communication, however, a thorough analysis indicates an existence of electronic charge delocalization between the ferrocenyl moiety and the central core. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Thiophene; Triarylamine; Sonogashira coupling; Electrochemistry

1. Introduction

Organometallic fragments assembled on substituted benzenes [1], polyaromatics, and heteroaromatics such as thiophenes [2] and pyridines [3] have received immense interest in recent years due to their potential use as models for organometallic polymers [4] and targets for the study of electron-transfer processes [5]. Also important, is the possibility that the mixed-valence materials derived from these multi-metallic systems, after partial oxidation, may exhibit unique magnetic properties [6]. We have earlier reported a series of homo- and hetero-bimetallic systems containing ferrocene and π-conjugated thienyl and furan moieties [7]. The electrochemistry of those derivatives revealed unique properties including the facile stabilization of thienyl or furanyl radical cations. In this paper, we describe a series of tri- or tetra-ferrocenes covalently attached to either triphenylamine or thiophene cores by a triple bond.

Triarylamines and polythiophenes are considered as important classes of compounds in materials science. Triarylamines, owing to their low oxidation potentials and easy glass-forming ability, are widely used as hole-transporting materials in organic light-emitting diodes [8]. Similarly, thiophenes because of their excellent electronic conducting properties find much use in the construction of opto-electronic devices [9]. In view of these advantages, we have utilized both triphenylamine and thiophene as the core unit for the construction of polyferrocenes. Palladium-catalyzed Sonogashira [10] coupling reactions were used for tailoring the units together by a triple bond. Even though these star-shaped molecules did not exhibit any intramolecular electronic communication among ferrocenes, the presence of ferrocene significantly affects the electrochemical behavior of the triphenylamine or thiophene core, and the extended conjugation by triphenylamine or thiophene makes the appended ferrocenes undergo comparatively facile oxidation.

2. Results and discussion

2.1. Syntheses and spectra of the polyferrocenes

A series of polyferrocenyl arenes were obtained previously using palladium-catalyzed cross-coupling reactions of ferrocenylzinc chloride with the corresponding di-, tri-, and tetra-halogenoarenes [11]. The Wittig reaction or McMurray coupling reactions involving the

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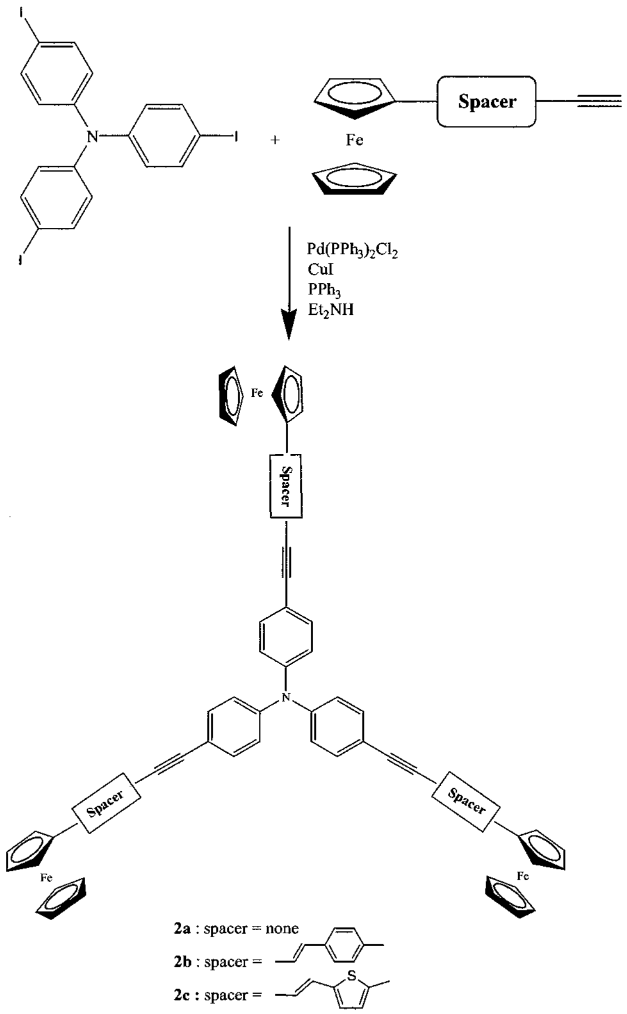
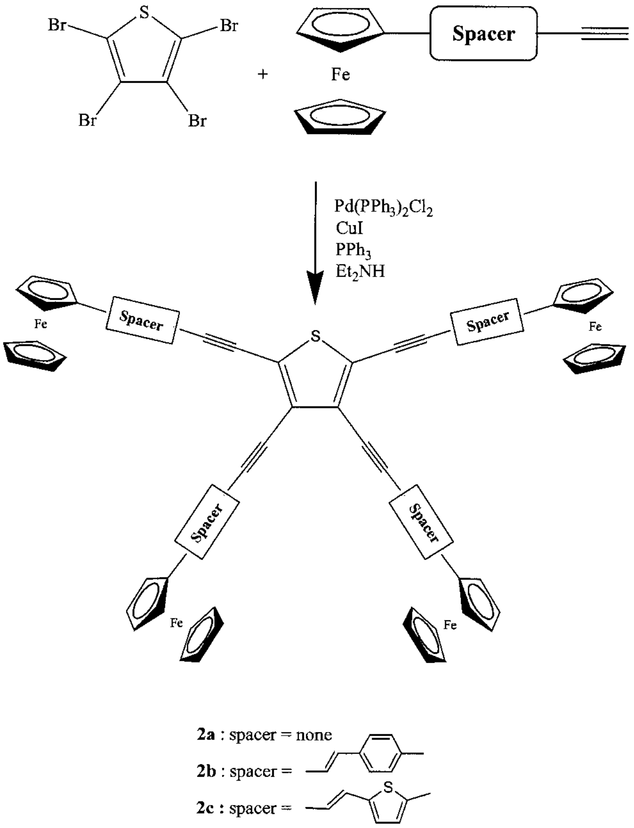
ferrocene carboxaldehyde with the suitable reagents provided the vinyl-separated diferrocenes and the possibility of extending this strategy to construct molecular wires was explored [12,7]. Similarly, the ethynyl linkage is normally achieved by the palladium-catalyzed Sonogashira coupling reactions. Di-, and tri-ferrocenyl derivatives were accessed using this later method [13,7]. In the present work, we use a similar procedure to assemble tri- and tetra-ferrocenenes on triphenylamine and thiophene cores. Thus, the triferrocenyl compounds (**2a**–**2c**) and the tetraferrocenyl thiophenes (**3a**–**3c**) were conveniently obtained by the palladium-catalyzed cross-coupling reactions of ferrocenyl alkynes (**1a**–**1c**) and 4,4′,4″-triiodotriphenylamine or 2,3,4,5-tetrabromothiophene in moderate to good yields (Schemes 1 and 2). To effect a complete conversion, we used slightly excess terminal alkynes in these reactions. The yellow to orange air-stable compounds are soluble in common chlorosolvents and insoluble in hexanes, however, the solubility slightly decreases on increasing the conjugation chain. Repeated attempts to grow X-ray quality crystals failed and only amorphous powders were obtained.



Scheme 1. Synthetic scheme for the synthesis of triphenylamine-based star-shaped triferrocenes.



Scheme 2. Synthetic scheme for the preparation of thiophene-based star-shaped tetraferrocenes.

The complexes were studied by routine spectroscopic and analytical methods (see experimental section for full details). Complexes **2a**–**2c** are symmetric in nature in solution as revealed by NMR spectroscopy. Only one set of signals corresponding to each ferrocenyl arm was observed. On the contrary, the complexes **3a**–**3c** are asymmetric in nature and they exhibited two types of signals. The two sets of signals could be assigned to the inequivalence in the thiophene 2- and 5- and 3- and 4-substituted segments. However, in the phenylene derivative **3b**, despite the presence of two sets of signals due to the vinyl and phenyl segments, only one set of signals attributable to the ferrocene moiety is observed. This may be due to the accidental isochronous chemical shifts triggered by the sensitivity of the measurements.

The electronic spectra of the complexes were measured in dichloromethane and the data with the tentative assignments are collected in Table 1. In general, the spectra of the complexes is dominated by a π–π* absorption band with a high absorption coefficient. They exhibit a weak low energy band attributable to the d–d transition arising from the ferrocene moiety [14]. An increase in conjugation length shifts the π–π* transitions to the lower energy and masks the d–d transitions if any. A similar, but more pronounced red shift is noticed when comparing the energies of the π–π* transitions in the free ferrocenyl acetylenes (**1a**–**1c**) with the corresponding triphenylamine derivatives (**2a**–**3c**) (Fig. 1).

Table 1
UV–vis data for the star-shaped compounds and the terminal alkynes

Complex	λ_{max}	ε_{max}	Assignment
1a	444	0.176	d–d
	264	6.08	π–π*
1b	461	2.25	d–d
	325	31.10	π–π*
	276	15.18	π–π* or n–π*
1c	469	2.94	d–d
	348	28.58	π–π*
2a	435	3.78	d–d
	371	77.68	π–π*
	297	39.33	π–π* or n–π*
2b	460	sh	d–d
	393	134.47	π–π*
	347	74.42	π–π* or n–π*
2c	480	sh	d–d
	409	114.86	π–π*
	346	sh	π–π*
3a	460	sh	d–d
	360	sh	π–π*
	309	27.44	π–π*
	271	26.76	π–π*
3b	480	sh	d–d
	430	sh	π–π*
	359	119.84	π–π*
3c	500	sh	d–d
	390	77.68	π–π*

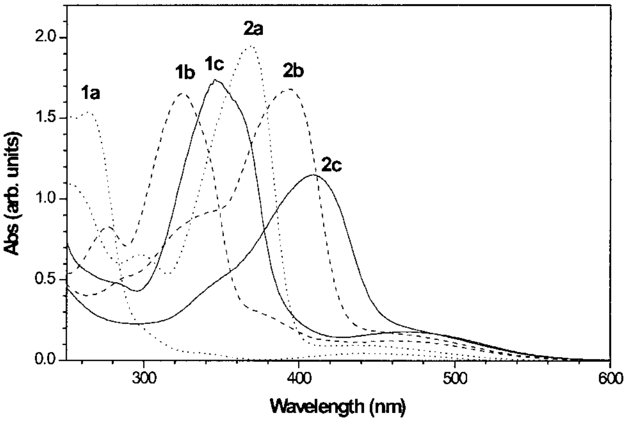


Fig. 1. Electronic spectra of the compounds **1a**–**1c** and **2a**–**2c**.

Table 2
Electrochemical data for the star-shaped compounds and the terminal alkynes

Compound	CV			OSWV
	$E_{1/2}$	ΔE_p	i^p_c/i^p_a	E_p
1a	148	96	0.952	148
1b	11	97	0.920	12
1c	16	93	0.964	16
2a	101	130	0.950	108
	778	i	–	716
	1018	i	–	952
2b	−5	113	0.940	0
	585	i	–	536
2c	6	129	0.947	12
	544	i	–	520
3a	134	98	0.932	140
	1061	i	–	1024
3b	−22	96	0.749	−20
	711	i	–	704
3c	−22	116	0.424	−12
	779	i	–	516

All the potentials are in mV and quoted with reference to the Fc/Fc$^+$ couple, which had a potential of 276 mV against the Ag/AgNO$_3$ non-aqueous reference electrode. All the measurements were carried out in dichloromethane solutions (10^{-3} M) with n-Bu$_4$NClO$_4$ (0.1 M) as the supporting electrolyte. Scan rate: 100 mV s^{-1}. i = irreversible.

2.2. Electrochemistry of the complexes

In order to investigate the possible intramolecular interaction of the three or four ferrocenyl groups, the complexes were examined by cyclic voltammetry (CV) and square wave voltammetry (OSWV). As summarized in Table 2, all compounds show reversible redox waves corresponding to the interconversion between ferrocene and ferricinium ion. The reversibility decreases for the thiophene derivatives as the conjugation length increases, which is evident from the i^c_p/i^a_p ratio. Only one wave is observed in all the compounds, reflecting the absence of electronic communication between the ferrocene centers. The lack of interaction between the ferrocene units in similar tri- and tetra-ferrocenyl systems has been noted previously [15]. For an efficient electronic communication, the nature of the chain length and the element type between the units are proven to be crucial. Tris(ferrocenes) such as 1,3,5-tris(-ferrocenylethynyl)benzene [15a], 1,3,5-triferrocenylbenzene [15b] and 1,2,4,5-tetraferrocenylbenzene [11] did not exhibit any observable electronic communication. On the contrary, tris(ferrocenes) anchored on cyclopropene [16] displayed separated one-electron-oxidation steps characteristic of strong interaction.

When compared to the free acetylenes (**1a**–**1c**), the oxidation potentials of the star-shaped compounds exhibit a slight cathodic shift. This ease in oxidation could be attributed to the electron-donating ability of the triphenylamine core in **2a**–**2c** and the extended conjugation in **3a**–**3c**. Similarly, within a series the short chain acetylene derivatives (**1a**, **2a** and **3a**) possess high oxidation potentials. This is clearly the result of the electron-withdrawing alkyne unit which directly connects the ferrocene segment [16]. This is further supported by the fact that among this series, **2a** displays a low oxidation potential due the countercharge donation from the triphenylamine core. In addition, all the polymetallic derivatives exhibit an irreversible anodic wave originating from the triphenylamine (**2a**–**2c**) or thiophene (**3a**–**3c**) segments. It is interesting to note that *para*-substituted triphenylamines undergo facile oxidation and produce stable cation radicals [17]. The irreversibility of the triphenylamine centered oxidation is mainly due to the destabilization forces contributed by the electron-withdrawing tris(ferricinium) ions generated by the oxidation of ferrocene moieties. The same argument can also be applied to thiophene oxidation. These suggestions are further supported by the fact that on increasing the conjugation length, a cathodic shift is observed for the oxidation wave due to the triphenylamine or thiophene cores. That is, on increasing the conjugation length, very little electronic perturbation reaches the central core.

3. Conclusions

We have successfully synthesized a series of star-shaped multi-metallic components featuring ferrocene, thiophene and triphenylamine by palladium-catalyzed ethynylation reactions. The lack of electronic communication between the ferrocene units in these tri- and tetra-metallic systems is attributed to the nature and length of the conjugation chain. However, a weak electronic interaction is witnessed between the ferrocene and the central cores (triphenylamine or thiophene).

4. Experimental

4.1. General

All the reactions were performed under a dry, oxygen-free nitrogen atmosphere; however, during the work-up, no precaution was taken to exclude air. Commercial-grade solvents were purified and dried according to the routine techniques. The starting materials, 2,3,4,5-tetrabromothiophene [18] and 4,4′,4″-triiodo-triphenylamine [19], were obtained according to the literature procedures. The syntheses of terminal alkynes **1b** and **1c** will be reported elsewhere. All other reagents were from commercial sources and used as received. The NMR spectra were recorded on a Bruker AC300 spectrometer. Optical electronic spectra were measured in CH_2Cl_2 using a Cary 50 Probe UV–vis spectrophotometer. Emission spectra were recorded by a Hitachi F-4500 fluorescence spectrometer. Cyclic voltammetry experiments were performed with a BAS-100 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a non-aqueous $Ag/AgNO_3$ reference electrode. The solvent in all experiments was CH_2Cl_2 and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. The $E_{1/2}$ values were determined as $1/2(E_{p(a)}+E_{p(c)})$, where $E_{p(a)}$ and $E_{p(c)}$ are the anodic and cathodic peak potentials, respectively. All potentials are reported relative to $Ag/AgNO_3$ and are not corrected for the junction potential. Fc^+/Fc was measured to be +0.220 V relative to $Ag/AgNO_3$. Mass spectra were obtained from a VG70-250S mass spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 CHN analyzer.

4.2. Syntheses of star-shaped ferrocenes **2a**–**3c**

Essentially the same conditions were employed for the multiple Sonogashiro coupling reactions leading to the star-shaped polyferrocenes **2a**–**3c**. So a representative procedure is given for **2a**. In a 250 ml Schlenk flask was added successively, 4,4′,4″-triiodo-triphenylamine (1 mmol), **1a** (4.0 mmol), bis(triphenylphosphine)dichloropalladium(II) (35 mg), cuprous iodide (5 mg), triphenylphosphine (26 mg) and diethylamine (30 ml). After refluxing the contents for 12 h, it was cooled and the volatiles were removed under vacuum to yield a brown residue. It was triturated with water and the solid was extracted into CH_2Cl_2. The organic extracts were thoroughly washed with brine solution and dried over anhydrous $MgSO_4$. After evaporation, the residue was adsorbed onto a silica gel and chromatographed using hexane–dichloromethane mixtures as the eluent to afford the desired product as the third prominent band in 76% yield. The first two bands were identified as **1a** and diferrocenylbutadiyne by comparison with authentic samples [20].

2a: Anal. Found: C, 74.82; H, 4.33; N, 1.58. Calc. for $C_{54}H_{39}Fe_3N$: C, 74.60; H, 4.52; N, 1.61%. FABMS (+ve); *m/z*: 869 [M^+]. ^{1}H-NMR(CD_2Cl_2, δ ppm): 4.21 (s, 15H, Cp); 4.26 (t, 1.8 Hz, 6H, Cp′); 4.48 (t, 1.7 Hz, 6H, Cp′); 7.06 (d, 8.5 Hz, 6H, Ph); 7.39 (d, 8.6 Hz, 6H, Ph). ^{13}C-NMR (CD_2Cl_2, δ ppm): 65.8 (Cp′); 69.2 (Cp′); 70.3 (Cp); 71.7 (Cp′); 85.8 (C≡C); 88.3 (C≡C); 118.9 (Ph); 124.4 (Ph); 132.8 (Ph); 146.7 (Ph).

2b: Anal. Found: C, 79.51; H, 5.01; N, 1.21. Calc. for $C_{78}H_{57}Fe_3N$: C, 79.67; H, 4.89; N, 1.19%. FABMS (+ve); *m/z*: 1175 [M^+]. ^{1}H-NMR (CD_2Cl_2, δ ppm): 4.14 (s, 15H, Cp); 4.32 (t, 1.7 Hz, 6H, Cp′); 4.49 (t, 1.7 Hz, 6H, Cp′); 6.71 (d, 16.1 Hz, 3H, vinyl); 6.95 (d, 16.1 Hz, 3H, vinyl); 7.09–7.12 (m, 6H, Ph); 7.41–7.49 (m, 18H, Ph). ^{13}C-NMR (CD_2Cl_2, δ ppm): 67.4 (Cp′); 69.65 (Cp); 69.7 (Cp′); 83.4 (Cp′); 89.9 ($C\equiv C$); 90.1 ($C\equiv C$); 118.5 (Ph, 3°); 121.7 (Ph, 3°); 124.5 (Ph); 125.5 (vinyl); 126.0 (Ph); 128.8 (vinyl); 132.1 (Ph); 133.1 (Ph); 138.4 (Ph, 3°); 147.1 (Ph, 3°).

2c: Anal. Found: C, 72.34; H, 4.40; N, 1.13. Calc. for $C_{72}H_{51}Fe_3NS_3$: C, 72.43; H, 4.31; N, 1.17%. FABMS (+ve); *m/z*: 1193 [M^+]. ^{1}H-NMR (CD_2Cl_2, δ ppm): 4.16 (s, 15H, Cp); 4.32 (t, 1.7 Hz, 6H, Cp′); 4.46 (t, 1.7 Hz, 6H, Cp′); 6.73 (d, 16.0 Hz, 3H, vinyl); 6.80 (d, 15.9 Hz, 3H, vinyl); 6.86 (d, 3.87 Hz, 3H, th); 7.10 (d, 8.6 Hz, 6H, Ph); 7.13 (d, 4.05 Hz, 3H, th); 7.44 (d, 8.5 Hz, 6H, Ph). ^{13}C-NMR (CD_2Cl_2, δ ppm): 67.4 (Cp′); 69.7 (Cp); 69.9 (Cp′); 82.8 (Cp′); 83.5 ($C\equiv C$); 94.0 ($C\equiv C$); 118.1 (th); 119.0 (th); 120.8 (Ph); 124.6 (Ph); 124.8 (vinyl); 128.9 (th); 132.9 (Ph); 133.0 (vinyl); 145.7 (th); 147.1 (Ph).

3a: Anal. Found: C, 68.29; H, 3.94. Calc. for $C_{52}H_{36}Fe_4S$: C, 68.16; H, 3.96%. FABMS (+ve); *m/z*: 916 [M^+]. ^{1}H-NMR (CD_2Cl_2, δ ppm): 4.23–4.27 (m, 28H, Cp and Cp′); 4.55 (t, 1.7 Hz, 4H, Cp′); 4.57 (t, 1.7 Hz, 4H, Cp′). ^{13}C-NMR (CD_2Cl_2, δ ppm): 64.0 (Cp′); 64.7 (Cp′); 68.6 (Cp′); 69.1 (Cp′); 70.3 (Cp); 71.8 (Cp); 78.1 ($C\equiv C$); 79.6 ($C\equiv C$); 94.4 ($C\equiv C$); 97.5 ($C\equiv C$); 124.5 (th); 127.8 (th).

3b: Anal. Found: C, 76.38; H, 4.62. Calc. for $C_{84}H_{60}Fe_4S$: C, 76.15; H, 4.56%. FABMS (+ve); *m/z*: 1325 [M^+]. ^{1}H-NMR (CD_2Cl_2, δ ppm): 4.14 (s, 20H, Cp); 4.30 (t, 1.8 Hz, 4H, Cp′); 4.47 (t, 1.7 Hz, 4H, Cp′); 6.68 (d, 16.0 Hz, 2H, vinyl); 6.69 (d, 16.1 Hz, 2H, vinyl); 6.94 (d, 16.2 Hz, 4H, vinyl); 7.43 (d, 7.5 Hz, 8H, Ph); 7.53 (d, 8.3 Hz, 4H, Ph); 7.56 (d, 8.5 Hz, 4H, Ph). ^{13}C-NMR (CD_2Cl_2, δ ppm): 67.1 (Cp′); 69.3 (Cp); 82.5 ($C\equiv C$); 82.8 (Cp′); 82.9 (Cp′); 83.8 ($C\equiv C$); 96.6 ($C\equiv C$); 99.3 ($C\equiv C$); 120.3 (Ph); 121.0 (Ph); 125.2 (th); 125.3 (Ph); 125.8 (vinyl); 128.1 (th); 128.6 (Ph); 128.9 (Ph); 132.0 (vinyl); 132.2 (vinyl); 138.3 (Ph); 138.6 (Ph).

3c: Anal. Found: C, 67.48; H, 3.78. Calc. for $C_{76}H_{52}Fe_4S_5$: C, 67.67; H, 3.89%. FABMS (+ve); *m/z*: 1348 [M^+]. ^{1}H-NMR (CD_2Cl_2, δ ppm): 4.12 (s, 10H, Cp); 4.14 (s, 10H, Cp); 4.30 (m, 8H, Cp′); 4.43 (m, 8H, Cp′); 6.74 (two overlapping AB quartets, 8H, vinyl); 6.87 (d, 3.5 Hz, 2H, th); 6.88 (d, 3.8 Hz, 2H, th); 7.23 (d, 3.6 Hz, 2H, th); 7.26 (d, 3.7 Hz, 2H, th). ^{13}C-NMR (CD_2Cl_2, δ ppm): 67.0 (Cp′); 69.3 (Cp); 69.4 (Cp′); 69.5 (Cp′); 82.3 (Cp′); 82.4 (Cp′); 86.2 ($C\equiv C$); 87.4 ($C\equiv C$); 90.4 ($C\equiv C$); 93.3 ($C\equiv C$); 118.6 (th); 118.7 (th); 119.2 (th); 119.9 (th); 124.4 (vinyl); 124.6 (vinyl); 128.8 (vinyl); 129.2 (vinyl); 133.7 (th); 124.0 (th); 146.2 (th); 146.8 (th).

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