

Synthesis of functionalized aryl-alkenes catalyzed by *CN-ortho*-palladated complex of 2,3-dimethoxybenzaldehyde oxime under microwave irradiation

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ABSTRACT

The catalytic activity of dimeric $[\text{Pd}\{\text{C}_6\text{H}_2(-\text{CH}=\text{NOH})-(\text{OMe})_{2,3}\}(\mu\text{-Cl})_2]$ complex as an efficient, air, and moisture tolerant catalyst was investigated in Mizoroki–Heck cross coupling reaction of various aryl halides and also arenesulfonyl chlorides with different coupling partner alkenes. The combination of homogenous metal catalyst, microwave irradiation, and microwave-active polar solvents gave high yields of functionalized aryl-alkene products in short reaction times.

Keywords: *ortho*-Palladated catalyst, Oxime palladacycle complexes, Heck reaction, Microwave irradiation.

1. Introduction

Transition metal catalyzed coupling reactions are among the most potent and convenient tools of modern organic synthesis [1]. Palladium is used as efficient and active catalyst in these reactions [2-4]. Generally, the combination of palladium catalysts with various phosphine ligands [5-8] and also *N*-heterocyclic carbenes (NHC) [9-11] results in excellent yields and high efficiency in cross-coupling reactions, however they are usually sensitive to air and moisture or expensive. Palladacycle complexes, with air and moisture-stability and high catalytic activity have recently been employed in cross-coupling reactions [12-15]. The high productivity of the palladacycle catalysts is due to the slow generation of low ligated Pd(0) complexes from a stable palladium(II) pre-catalyst [16].

Among the various cross coupling reactions Heck coupling that described as olefin arylation, is one of the most promising palladium catalyzed C–C bond formation reactions for synthesis of monomers, pharmaceuticals, sunscreen agents, herbicides and high performance materials [17-20]. The most researches have performed considerable efforts to find new catalytic systems and methodologies to improve Heck coupling reaction conditions.

Transition-metal-catalyzed cross-coupling reactions typically need long reaction times and an inert atmosphere to reach completion with traditional heating. Modern techniques are focused on the design of novel methodologies to modify these chemical transformations using simpler, faster, and more efficient processes. The use of microwave irradiation in homogeneous transition metal-catalyzed reactions leads to the reduction of reaction times, production of high yields and higher selectivity, the decrease of discarded byproducts from thermal side-reactions, and increased lifetime of the catalyst [21-23].

In continuation of our recent investigations on the synthesis of the palladacycle catalysts and application of these complexes in microwave assisted cross coupling reactions [24-26], we now wish to report the synthesis and the extension of $[\text{Pd}\{\text{C}_6\text{H}_2(-\text{CH}=\text{NOH})-(\text{OMe})_{2,3}\}(\mu\text{-Cl})_2]$ homogeneous complex, as a thermally stable and oxygen insensitive catalyst for the Heck cross-coupling reaction of various aryl halides under microwave irradiation.

2. Experimental

2.1. Reagents and measurements

All melting points were taken on a Gallenkamp melting apparatus. ¹H-NMR spectra were recorded using 400 MHz in CDCl₃ solutions at room temperature (TMS was used as an internal standard) on

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a Bruker, Avance 500 instrument (Rheinstetten, Germany) and Varian 400 NMR. FT-IR spectra were recorded on a spectrophotometer (Jasco-680, Japan). Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies were reported in a wave number (cm^{-1}). We used the Milestone microwave (Microwave Labstation- MLS GmbH-ATC-FO 300) for synthesis. Furthermore, we used GC (BEIFIN 3420 Gas Chromatograph equipped a Varian CP SIL 5CB column- 30 m, 0.32 mm, 0.25 μm) for examination of reaction completion and yields. Palladium chloride, aryl halides and all chemicals were purchased from Merck and Aldrich and were used as received.

2.2. General procedure for the synthesis of *ortho*-palladated oxime complex

2,3-Dimethoxybenzaldehyde oxime was synthesized according to our previous work [26]. For the synthesis of *ortho*-palladated oxime complex, to a solution containing PdCl_2 (1 mmol) and 2 mmol LiCl in methanol (40 mL), a methanol solution of 2,3-dimethoxybenzaldehyde oxime (1 mmol) and sodium acetate (1 mmol) was added. The mixture was stirred for 48 h at room temperature. Then the mixture was filtered and water (30 mL) was added to the filtrate to give yellow solid. The residue was recrystallized from dichloromethane to give catalyst (A) (53%). Elemental analysis ($\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_6\text{Cl}_2\text{Pd}_2$); calculated: C 33.56, H 3.13, N 4.35. Found: C 33.62, H 3.12, N 4.30. m.p.= 186 °C (dec). ^1H NMR (500 MHz, CDCl_3): = 8.72 (s, 1H), 8.46 (s, 1H), 6.91 (d, $^3J= 8.8$ Hz, 1H), 6.85 (d, $^3J= 8.8$ Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H) ppm. FT-IR (KBr): $\bar{\nu} = 3400, 3000, 1650, 1600, 1560, 1510, 1450 \text{ cm}^{-1}$.

2.3 General procedure for the synthesis of functionalized aryl-alkenes

In a round-bottom flask equipped with a magnetic stirring bar to a mixture of K_2CO_3 (1.1 mmol), olefin (2.2 mmol) and aryl halide (1 mmol) in *N*-methyl-2-pyrrolidone (NMP) (3 mL) were added 0.05 mol% of CN-*ortho*-palladated complex (A) and equipped with a condenser for refluxing in microwave irradiation. Initially the microwave irradiation was set at 500 W

and the temperature was ramped from room temperature to the desired temperature of 120 °C. Once this was reached, the reaction mixture was held at this temperature until the reaction was completed. During this time, the power was modulated automatically to keep the reaction mixture at 120 °C. The mixture was stirred continuously during the reaction. The reaction progress was followed by TLC (hexane/EtOAc, 85:15, as eluent) and gas chromatography (GC). After completion of the reaction, the mixture was cooled to room temperature and was diluted with ether and water. Then the organic layer was washed with brine, dried over MgSO_4 , filtered and evaporated under reduced pressure using rotary evaporator to give the crude product that was purified by recrystallization from ethanol.

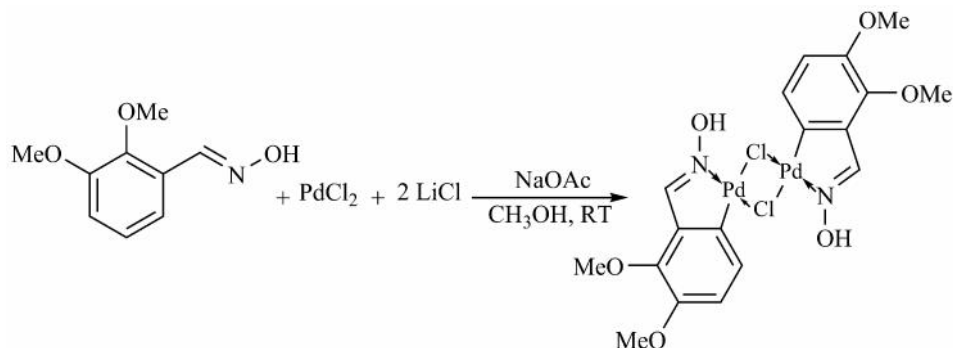
The products were characterized by comparing their m.p., IR, ^1H and ^{13}C NMR spectra with those found in the literature [28-32].

Methyl *trans* 4-formylcinnamate was obtained as a white solid; m.p.= 81-83 °C. ^1H NMR (400 MHz, CDCl_3): = 10.10 (s, 1H), 7.92 (d, $^3J= 8.4$ Hz, 2H), 7.71 (d, $^3J= 15.6$ Hz, 1H), 7.66 (d, $^3J= 8.2$ Hz, 2H), 6.57 (d, $^3J= 15.8$ Hz, 1H), 3.85 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): = 191.3, 168.8, 143.1, 140.0, 137.2, 130.2, 130.1, 128.3, 128.0, 121.0, 52.5 ppm. FT-IR (KBr): $\bar{\nu} = 3034, 2940, 2750, 1725, 1710 \text{ cm}^{-1}$.

3. Results and Discussion

In this paper, dimeric CN-*ortho*-palladate complex [$\text{Pd}\{\text{C}_6\text{H}_2(-\text{CH}=\text{NOH})(-\text{OMe})_{2-2,3}\}(\mu\text{-Cl})_2$] (A) was synthesized (Scheme 1) and the efficiency of this catalyst was investigated in Heck cross coupling reaction of various aryl halides under microwave irradiation.

In FT-IR spectra the OH and C=NOH group were observed around 3400 and 1510 cm^{-1} . Palladacycle complexes are homogeneous catalysts. The structure of this type of catalysts was elucidated in some of published papers and stereochemistry of the complexes was confirmed [33-34]. In palladacycle catalysts such as oxime palladacycle, palladium was connected to carbon of the aromatic ring *via* covalently bond.



Scheme 1. Preparation of CN-*ortho*-palladated catalyst.

Absence of signal of *ortho* proton to the nitrogen in NMR data, for example in *ortho*-palladated complexes were synthesized in our research group [28-30] and X-ray crystallographic data of dimeric and monomeric complexes in literatures [33] were proofed the structure of these catalysts and shown oxidation degree of the Pd is +2.

In order to optimize the reaction conditions vinylation of 4-bromoacetophenone with methyl methacrylate carried out using catalyst (A) as the catalyst in various solvents and organic and inorganic bases under microwave irradiation, as shown in Table 1.

The monitoring system for reaction times, temperature, pressure, and power in microwave reactor allow for an excellent control of reaction parameters which generally leads to rapid optimization and more reproducible reaction conditions. The direct control of reaction mixture temperature; carry out with the IR sensors. The best results were obtained in NMP as the high microwave absorbing solvent and K₂CO₃ as base by employing 0.05 mol% of *ortho*-palladated complex (A) as the catalyst at 120 °C and 500 W (Table 1, entry 7). As this catalyst is not sensitive to oxygen, the

reactions were carried out under air atmosphere. These optimize reaction conditions were applied in the Heck cross-coupling reaction of various aryl halides under microwave irradiation (Scheme 2).

As is demonstrated in Table 2, the catalyst can be used for coupling reaction of aryl iodides, bromides and even less reactive aryl chlorides and also arenesulfonyl chlorides with methylacrylate, methylmetacrylate and styrene in good to excellent yields (Table 2).

We examined the electronic and steric effects on the resulted yields and conversion times of the reactions. The results listed in Table 2 clearly showed that the coupling reactions with methylacrylate as the olefin were faster than styrene. In the case of 1-bromo-3-chlorobenzene, although this procedure could active C-Cl bond, however by using stoichiometric amount of olefins only the Br was substituted in each case that may be due to the higher activity of Br in compare to Cl. In all of the reactions, only the *trans* isomers were produced. The formation of functionalized aryl-alkenes in *trans* form was proved by ¹HNMR, coupling constant (³J) in *trans* hydrogens is about 16 Hz.

Table 1. Optimization of reaction conditions under microwave irradiation.^a

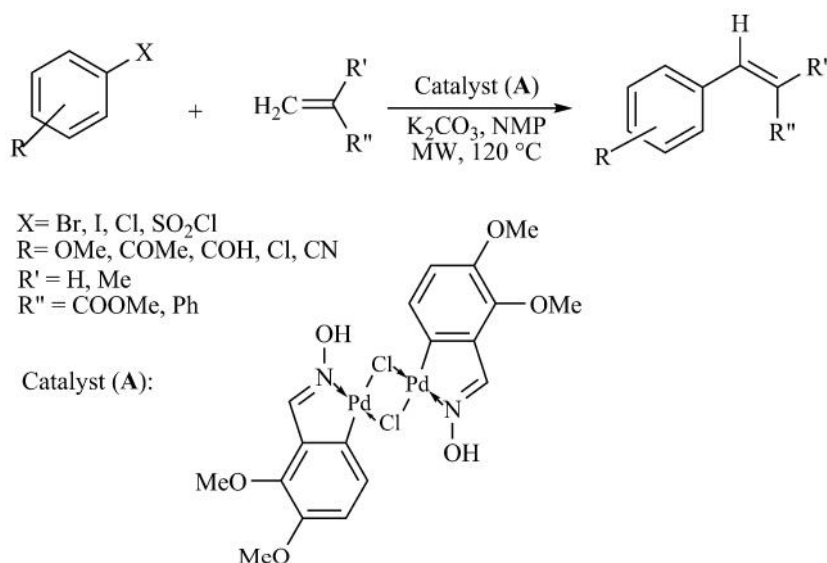
Entry	Solvent	Base	Catalyst (mol%)	Temperature (°C)	Conversion (%) ^b
1	NMP	Et ₃ N	0.1	120	5
2	NMP	Cs ₂ CO ₃	0.1	120	40
3	NMP	Na ₂ CO ₃	0.1	120	75
4	NMP	CH ₃ COONa	0.1	120	80
5	NMP	K ₂ CO ₃	0.1	120	100
6	NMP	K ₂ CO ₃	0.1	100	90
7	NMP	K ₂ CO ₃	0.05	120	100
8	NMP	K ₂ CO ₃	0.04	120	92
9	NMP	K ₂ CO ₃	0.2	120	100
10	DMF	K ₂ CO ₃	0.1	120	90
11	DMAc	K ₂ CO ₃	0.1	120	34
12	DMSO	K ₂ CO ₃	0.1	110	18
13	CH ₃ CN	K ₂ CO ₃	0.1	80	0
14	Toluene	K ₂ CO ₃	0.1	110	0
15 ^c	NMP	K ₂ CO ₃	0.2	120	95
16 ^d	NMP	K ₂ CO ₃	0.2	120	100

^aReaction conditions: 4-bromoacetophenone (1 mmol), methylacrylate (2.2 mmol) base (1.1 mmol), solvent (2 mL), catalyst (A), 500 W, 5 min.

^bDetermined by GC based on the ArX using decane as internal standard over the crude reaction mixture.

^cPower of microwave irradiation was regulated on 400 W.

^dPower of microwave irradiation was regulated on 600 W.



Scheme 2. The Heck cross-coupling reaction by CN-*ortho*-palladated catalyst.

The most reported catalyst need to be used in high loadings and they show little or no activity with aryl chloride substrates. The ideal substrates for coupling reactions are aryl chlorides since they tend to be cheaper and more widely available than their bromide or iodide counterparts. Unfortunately the high C-Cl bond strength compared with C-Br and C-I bonds disfavors oxidative addition, the first step in catalytic coupling reactions. Furthermore as shown in Table 2 (entries 10-12 and 21-23) the CN-*ortho*-palladated catalyst (A) can be used in the Heck coupling of even less reactive aryl chloride derivatives with olefines with longer reaction times.

Arenesulfonyl chlorides could be used as electrophilic partners under desulfonylation conditions in place of arylhalides (Table 2, entry 13 and 24-25). Arenesulfonyl chlorides are inexpensive and readily available compounds and more reactive than corresponding bromides and chlorides.

Since oxime *ortho*-palladated complex is a homogenous catalyst, therefore the recyclability of this catalytic system is not investigated, however the load of palladacycle catalyst in this cross coupling reaction is low amount (0.05 mol%).

Study on palladacycle catalyst cross-couplings showed that the catalyst role in these reactions is probably involve the palladium nanoparticles and palladacycles behave as a mere resource for producing nanoparticles Pd(0) [35-37]. Palladacycles decompose to liberate catalytic Pd(0) species and show a positive Hg(0) test which was assigned as probable evidence for catalysis by Pd nanoparticles [38]. To evaluate the proposed mechanism, the mercury drop test was operated. In the

presence of a heterogeneous catalyst, mercury leads to the amalgamation of the surface of it. In contrast, Hg(0) cannot have a poisoning effect on homogeneous palladium complexes, where the Pd(II) metal centre is tightly bound to the ligand. When a drop of Hg(0) was added to the reaction mixture under mentioned optimized conditions and heated the reaction mixture, no catalytic activity was observed for the catalyst.

A general catalytic cycle for the Heck cross coupling reaction using the palladium catalyst has been presented in Scheme 3. The reaction may occur *via* oxidative addition, insertion, hydride elimination and then reductive elimination by removal of hydrogen halide with base providing the cross coupled product and Pd (0).

A short glimpse to the results listed in Table 2 in comparison to Table 3 indicates that using microwave irradiation not only reduces the reaction times, but also increases the yields of the reactions. The dramatic rate enhancement is due to the rapid and uniform heating of the reaction mixture and increased catalyst lifetime by the elimination of wall effects in microwave versus oil-bath heating. Microwave irradiation raises the temperature of the whole volume simultaneously (bulk heating) whereas in the oil-heated tube, the reaction mixture in contact with the vessel wall is heated first [23].

To investigate the efficiency of *ortho*-palladated complex (A), the formation of *trans*-4-acetylstilbene was considered and this catalytic system is compared with other palladium based catalytic systems. As can be seen in Table 4, this CN-*ortho*-palladated oxime complex gave better yield in shorter time [28, 39-41].

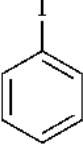
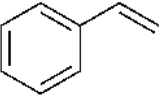
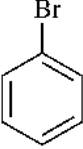
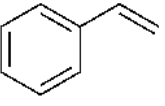
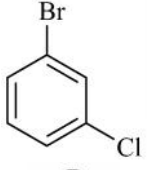
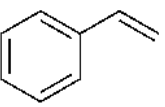
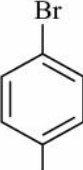
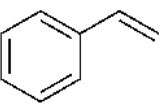
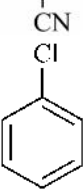
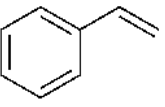
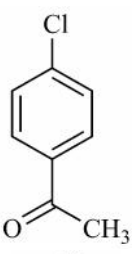
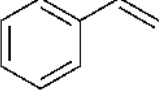
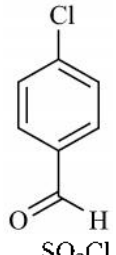
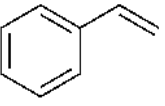
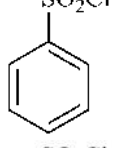
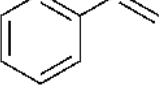
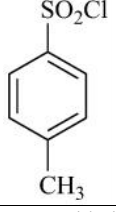
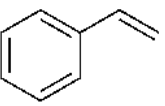
Table 2. Arylation of olefins catalyzed by CN-*ortho*-palladated catalyst (A) under microwave irradiation.^a

Entry	ArX	R''R'C=CH ₂	Time (min)	Yield (%) ^b	m.p. (°C)		Ref.
					Found	Reported	
1			1	93	34-36	34-37	[27]
2			2	94	34-36	34-37	[27]
3			4	90	82-84	82-84	[30]
4			4	96	86-88	87-89	[28]
5			2	95	Oil	-	[30]
6			3	95	116-118	118-120	[27]
7			4	93	31-33	30-33	[27]

Table 2. (Continued).

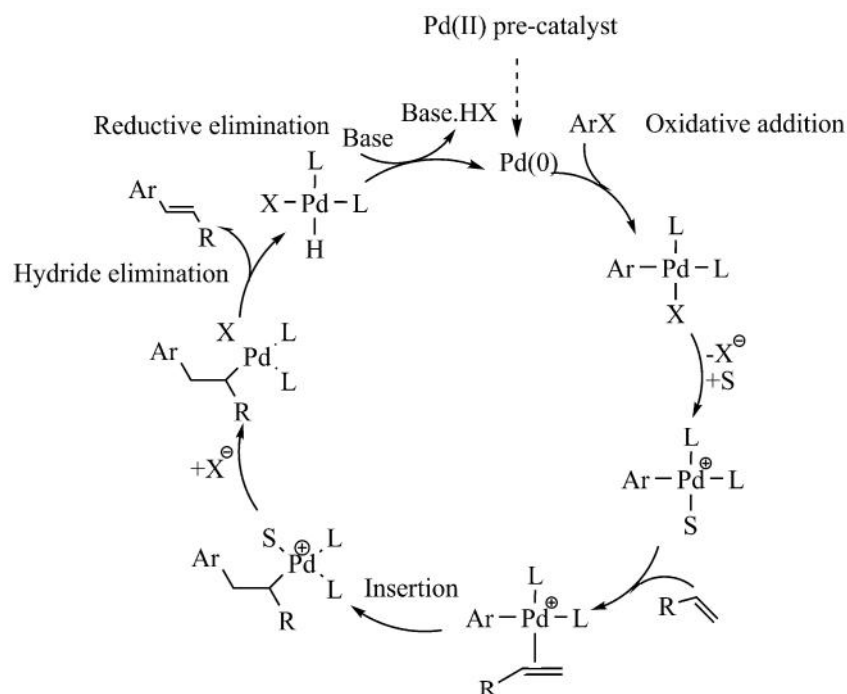
8			6	90	Oil	-	[27]
9			9	88	Oil	-	[28]
10			7	90	34-36	34-37	[27]
11			6	89	31-33	30-33	[27]
12			6	90	82-84	82-84	[30]
13			5	94	34-36	34-37	[27]
14			2	94	Oil	-	[29]
15			3	94	Oil	-	[29]
16			6	91	Oil	-	[29]

Table 2. (Continued).

17			3	93	122-123	121-122	[30]
18			5	90	122-123	121-122	[30]
19			4	93	66-68	64-69	[30]
20			5	92	116-117	114-117	[30]
21			12	84	122-123	121-122	[30]
22			10	80	138-140	138-141	[30]
23			8	78	111-113	111-112	[31]
24			8	92	122-123	121-122	[30]
25			10	76	120-122	120-122	[27,32]

^aReaction conditions: aryl halide (1 mmol), olefin (2.2 mmol), K₂CO₃ (1.1 mmol), catalyst (A) (0.05 mol%), NMP; 120 °C, MW, 500 W.

^bIsolated yield.



Scheme 3. Proposed mechanism for the Heck cross coupling reaction.

4. Conclusions

In this work, a general protocol was applied for the microwave-promoted Heck coupling reaction using CN-*ortho*-palladated complex of 2,3-dimethoxybenzaldehyde oxime. The catalytic amounts of this dimeric complex as an inherent air and moisture resistances catalyst converted various aryl halides to the functionalized aryl-alkenes in excellent yields. The combination of homogenous complex as catalyst, microwave irradiation and microwave-active polar solvent caused to increase lifetime of the catalyst, improve the yields of the reactions and decrease the reaction times.

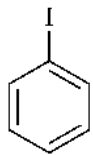
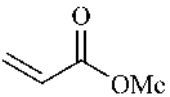
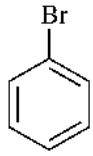
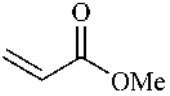

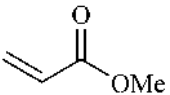
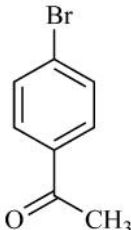
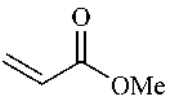

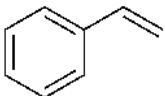
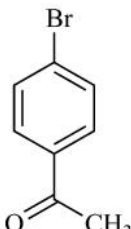
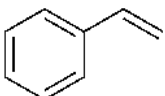
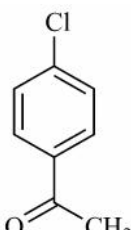
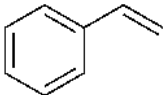
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Table 3. Arylation of olefins catalyzed by CN-*ortho*-palladated catalyst (**A**) under conventional heating conditions using an oil bath.^a

Entry	ArX	Olefine	Time (min)	Yield (%) ^b
1			18	91
2			25	90
3			30	92
4			40	91
5			100	90
6			90	92
7			180	78

^aReaction conditions: aryl halide (1 mmol), olefin (2.2 mmol), K₂CO₃ (1.1mmol), catalyst (**A**) (0.05 mol%), NMP, 120 °C, oil bath.^bIsolated yield.

Table 4. Comparison of various catalysts in cross coupling reaction of 4-acetylbromobenzene with styrene under conventional heating conditions.

Entry	Catalytic system	Solvent Temp. (°C)	Time (h)	Yield (%)	Ref.
1		120	10	72	[39]
2		DMF, 125	24	82	[40]
3		DMAc, 130	16	52	[41]
4		DMAc, 130	72	86	[41]
5		NMP, 130	10	80	[28]
6		NMP, 130	1:30	92	This work

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