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Formation of nitriles by a novel metathesis reaction of ruthenium σ-acetylide complexes, (η^5-indenyl)Ru(η^1-C≡CR)(phosphine)$_2$, with nitric oxide

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Abstract

(η^5-In)Ru(η^1-C≡CPh)(PPh_3)$_2$ (In = indenyl) treated with nitric oxide (1 atm) in the presence of $NaClO_4$ gave [(η^5-In)Ru(CO)(PPh_3)$_2$]$ClO_4 \cdot 0.5CH_2Cl_2$ and benzonitrile (PhC≡N) in good yields, through a novel metathesis reaction between σ-acetylide and NO. (η^6-C_6Me_6)Ru(η^1-C≡CPh)(PPh_3)Cl also readily underwent the metathesis reaction with NO to afford benzonitrile.

Key words: Ruthenium; Nitrosyl; Indenyl; Metathesis

Nitric oxide is a well-known atmospheric pollutant and new ways to convert it into useful chemical compounds have been the subject of considerable attention. The direct decomposition and reduction of NO, catalyzed by metallosilicates, have been extensively studied with respect to the removal of nitrogen oxides from air [1]. Further, a wide variety of transition metal complexes containing nitrosyl ligand has been prepared [2], and the transformations of bound nitrosyl groups by protonation [3], carbanion reduction [4], and migratory insertion [5] have been reported. During our investigation of indenyl complexes of isocyanides [6], we unexpectedly found an efficient formation of nitriles by a metathesis reaction of the ruthenium σ-acetylide complex, (η^5-In)Ru(η^1-C≡CR)(phosphine)$_2$ (In = indenyl), with NO.

(η^5-In)Ru(η^1-C≡CR)(PPh_3)$_2$ (R = Ph (**1a**), *p*-Tol (**1b**), ^{n}Bu (**1c**), and Cy (**1d**)) were prepared by the method of Oro *et al.* [7], and (η^5-In)Ru(η^1-C≡CPh)(diphos) (diphos = 1,2-bis(diphenylphosphino)ethane (dppe) (**2a**), 1,2-bis(diphenylphosphino)propane (dppp) (**2b**), and 1,4-bis(diphenylphosphino)butane (dppb) (**2c**)) were prepared by the reaction of (η^5-In)RuCl(diphos) with phenylacetylene in the presence of alcoholic KOH [8*]. The IR spectra of **1** and **2** showed a peak corresponding to ν(C≡C) at 2070–2100 cm^{-1}. In the ^{1}H NMR spectra, an AX_2 pattern for five-membered indenyl ring protons was observed at δ 4.4–5.0 (d, H1, 3) and δ 5.0–5.4 (t, H2). The structure of **2a** was confirmed by X-ray crystallography (Fig. 1) [9*], which is similar to that of (η^5-C_5H_5)Ru(η^1-C≡CPh)(dppe) (**3**) [10]. The η^5-indenyl group coordinates to the metal with a slight slippage toward the η^3-mode, the bond distance of indenyl carbon–metal ranging from 2.210(7) to 2.352(8) Å. The linear phenylacetylide moiety attaches to the ruthenium with Ru(1)–C(11)–C(12) = 174.9(6)° and C(11)–C(12)–C(13) = 175.7(8)°. The Ru(1)–C(11) and C(11)–C(12) bond distances are 2.033(7) and 1.200(9) Å; the former is slightly longer than that of **3**.

When (η^5-In)Ru(η^1-C≡CPh)(PPh_3)$_2$ (**1a**) in dichloromethane was treated with NO (1 atm) in the presence of $NaClO_4$ at room temperature for 15 min, benzonitrile (PhC≡N) was obtained quantitatively, and the subsequent work-up gave [(η^5-In)Ru(CO)(PPh_3)$_2$]$ClO_4 \cdot 0.5CH_2Cl_2$ [7] in 80% yield. Formation of nitrile proceeded in benzene, tetrahydrofuran, and dimethylformamide as well as in dichloromethane in

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* Reference number with asterisk indicates a note in the list of references.

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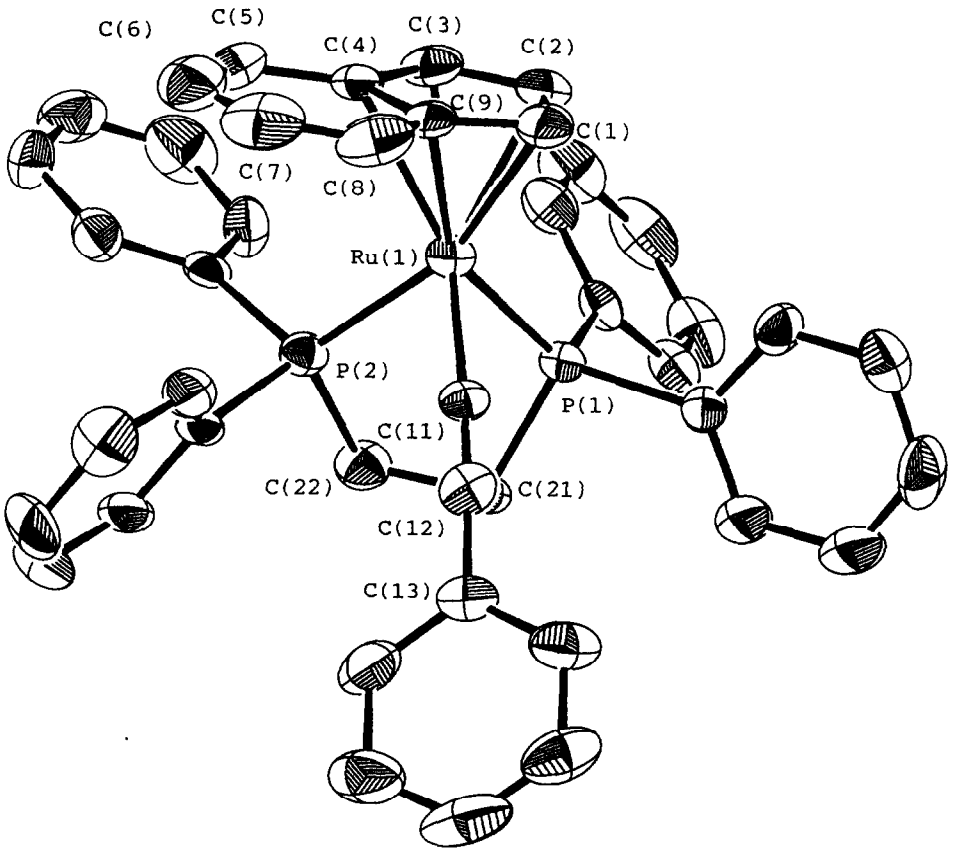


Fig. 1. A perspective drawing of **2a**. Some selected bond lengths (Å): Ru(1)–P(1) = 2.232(2), Ru(1)–P(2) = 2.277(2), Ru(1)–C(1) = 2.239(8), Ru(1)–C(2) = 2.210(7), Ru(1)–C(3) = 2.265(8), Ru(1)–C(4) = 2.352(8), Ru(1)–C(9) = 2.335(8), Ru(1)–C(11) = 2.033(7), C(11)–C(12) = 1.200(9), and C(12)–C(13) = 1.42(1), and some selected bond angles (°): P(1)–Ru(1)–P(2) = 83.99(8), P(1)–Ru(1)–C(11) = 81.2(2), P(2)–Ru(1)–C(11) = 83.8(2), Ru(1)–C(11)–C(12) = 174.9(6), and C(11)–C(12)–C(13) = 175.7(8).

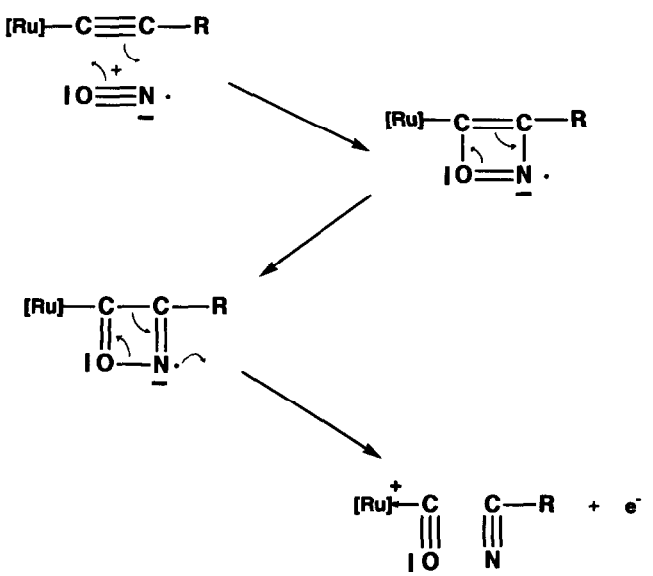
TABLE 1. Yields of nitriles derived from the reaction of σ-acetylide complexes with NO

Complexes	Conditions [a]	Yield of RCN (%) [b]	R
1a	$NaClO_4/CH_2Cl_2$	100	Ph
1a	$NaClO_4$/THF	81	Ph
1a	$NaClO_4$/benzene	63	Ph
1a	$NaClO_4$/DMF	66	Ph
1a	CH_2Cl_2	73	Ph
1a	THF	74	Ph
1a	benzene	65	Ph
1b	$NaClO_4/CH_2Cl_2$	90	*p*-Td
1c	$NaClO_4/CH_2Cl_2$	98	^{n}Bu
1d	$NaClO_4/CH_2Cl_2$	41	Cy
2a	$NaClO_4/CH_2Cl_2$	97	Ph
2b	$NaClO_4/CH_2Cl_2$	67	Ph
2c	$NaClO_4/CH_2Cl_2$	73	Ph
$Cu(C{\equiv}CPh)(PPh_3)$	$NaClO_4/CH_2Cl_2$	trace	Ph
trans-$Pd(C{\equiv}CPh)_2(PPh_3)_2$	$NaClO_4/CH_2Cl_2$	trace	Ph
trans-$Pd(C{\equiv}CPh)_2(PPh_3)_2$	$NaClO_4/CH_2Cl_2$	trace	Ph
$Rh(C{\equiv}CPh)(CO)(PPh_3)_2$	$NaClO_4/CH_2Cl_2$	trace	Ph
$RuH(CO)(C{\equiv}CPh)(PPh_3)_3$	$NaClO_4/CH_2Cl_2$	trace	Ph
$(\eta^5\text{-}C_5H_5)Ru(C{\equiv}CPh)(PPh_3)_2$	$NaClO_4/CH_2Cl_2$	42	Ph
$(\eta^5\text{-}C_5H_5)Fe(C{\equiv}CPh)(CO)_2$	$NaClO_4/CH_2Cl_2$	31	Ph
$(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CPh)(PPh_3)Cl$	$NaClO_4/CH_2Cl_2$	92	Ph
$(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CPh)(PPh_3)Cl$	CH_2Cl_2	80	Ph

[a] Room temperature, 15 min. [b] Based on metal.

the presence or absence of $NaClO_4$ (Table 1). In the absence of $NaClO_4$, the counter anion for $[(\eta^5\text{-In})Ru(CO)(PPh_3)_2]^+$ was not determined. Complexes **1b** and **1c** treated with NO gave corresponding nitriles in good yields; however, the yield of cyclohexylnitrile from **1d** was suppressed to 41%, probably due to the steric bulk of the cyclohexyl group. The present reaction is regarded as a novel metathesis reaction between acetylide moiety and nitric oxide, and the remarkable aspect is the extremely mild set of conditions required for the reaction (the short reaction time, room temperature, and the low, 1 atm, pressure of nitric oxide). $(\eta^5\text{-In})Ru(\eta^1\text{-C}{\equiv}CPh)$(diphos) (**2a**: dppe, **2b**: dppp, **2c**: dppb) readily underwent metathesis with NO to yield benzonitrile in good yields, suggesting that the reaction does not involve dissociation of phosphine ligand.

It was concluded that NO reacts directly with the acetylide part rather than with the ruthenium centre, and that the bulky indenyl and phosphine ligands serve to protect the metal centre against NO. The yields of benzonitrile were seriously suppressed (10–30%) by the reaction of **1a** with NO in the presence of *p*-benzoquinone as a radical scavenger and that with $NOBF_4$. Further, the reaction of **1a** with $NOBF_4$ in the presence of *p*-benzoquinone yielded only a trace of benzonitrile. The NO radical is the reactive species of the present metathesis. A plausible mechanism is depicted in Scheme 1, in which the metathesis proceeds via a cyclic intermediate reminiscent of the cycloaddition of



Scheme 1. [Ru] = $(\eta^5\text{-In})Ru(PPh_3)_2$.

$(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-C}{\equiv}CPh)(PPh_3)_2$ with tetracyanoethylene [11].

Other transition metal complexes of σ-phenylacetylide were examined (Table 1). $(\eta^6\text{-}C_6Me_6)Ru(\eta^1\text{-C}{\equiv}CPh)(PPh_3)Cl$ (**4**) [12 *] readily underwent the metathesis reaction with NO to afford benzonitrile (80–92%), whereas $(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-C}{\equiv}CPh)(PPh_3)_2$ and $(\eta^5\text{-}C_5H_5)Fe(\eta^1\text{-C}{\equiv}CPh)(CO)_2$ reacted with NO to give benzonitrile in lower yields (42 and 31%) than those of **1a** and **4**. Further, the σ-phenylacetylide complexes without cyclopentadienyl ligand, $Cu(\eta^1\text{-C}{\equiv}CPh)(PPh_3)$, *trans*-$Pd(\eta^1\text{-C}{\equiv}CPh)_2(PPh_3)_2$, *trans*-$Pt(\eta^1\text{-C}{\equiv}CPh)_2(PPh_3)_2$, $Rh(\eta^1\text{-C}{\equiv}CPh)(CO)(PPh_3)_2$, and $RuH(CO)(\eta^1\text{-C}{\equiv}CPh)(PPh_3)_3$ [13], showed almost no activity. The η^5-indenyl and η^6-hexamethyl benzene ligand might play an important role in the present metathesis reaction.

Acknowledgment

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8 Complexes **1b–1d** were prepared by a method similar to that for **1a**.
$(\eta^5\text{-In})Ru(\eta^1\text{-C}{\equiv}C(p\text{-Tol}))(PPh_3)_2\cdot 0.5CH_2Cl_2$ (**1b**): Yield 51%. Calcd. for $C_{54.5}H_{45}RuP_2Cl$: C, 72.86; H, 5.05. Found: C, 73.90; H, 5.05%. IR (Nujol): ν(C≡C) 2072 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.25 (s, *p*-CH_3), 4.51 (d, H1, 3 of In), 5.31 (t, H2 of In).
$(\eta^5\text{-In})Ru(\eta^1\text{-C}{\equiv}C^nBu)(PPh_3)_2\cdot 0.5CH_2Cl_2$ (**1c**): Yield 77%. Calcd. for $C_{51.5}H_{47}RuP_2Cl$: C, 71.56; H, 5.48. Found: C, 71.16; H, 5.74%. IR (Nujol): ν(C≡C) 2103 cm^{-1}. ^1H NMR ($CDCl_3$): δ

0.8 (m, CH_3), 1.30–2.40 (m, CH_2), 4.50 (d, H1, 3 of In), 5.38 (t, H2 of In).

(η^5-In)Ru(η^1-C≡CCy)(PPh_3)$_2$·CH_2Cl_2 (**1d**): Yield 78%. Calcd. for $C_{54}H_{50}RuP_2Cl_2$: C, 69.52; H, 5.40. Found: C, 70.49; H, 5.39%. IR (Nujol): ν(C≡C) 2101 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.0 ~ 2.0 (m, Cy), 4.45 (d, H1, 3 of In), 5.22 (t, H2 of In).

(η^5-In)Ru(η^1-C≡CPh)(dppe)·0.5CH_2Cl_2 (**2a**): Yield 34%. Calcd. for $C_{43.5}H_{37}RuP_2Cl$: C, 68.91; H, 4.92. Found; C, 67.74; H, 4.84%. IR (Nujol): ν(C≡C) 2078 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.0–2.6 (m, CH_2), 5.04 (d, H1, 3 of In), 5.22 (t, H2 of In).

(η^5-In)Ru(η^1-C≡CPh)(dppp)·0.5CH_2Cl_2 (**2b**): Yield 35%. Calcd. for $C_{44.5}H_{39}RuP_2Cl$: C, 69.21; H, 5.09. Found: C, 69.80; H, 5.11%. IR (Nujol): ν(C≡C) 2070 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.3–3.0 (m, CH_2), 4.69 (d, H1, 3 of In), 5.02 (t, H2 of In).

(η^5-In)Ru(η^1-C≡CPh)(dppb)·0.5CH_2Cl_2 (**2c**): Yield 90%. Calcd. for $C_{45.5}H_{41}RuP_2Cl$: C, 69.50; H, 5.26. Found: C, 70.17; H, 5.24%. IR (Nujol): ν(C≡C) 2070 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.3–3.4 (m, CH_2), 4.51 (d, H1, 3 of In), 5.39 (t, H2 of In).

9 Recrystallization of **2a** from a THF-hexane mixed solvent gave crystals suitable for crystallography. An orange crystal (0.52×0.45 ×0.27 mm) sealed into 0.7 mm glass-tube capillary was used in the intensity data collection on a Rigaku AFC5S diffractometer with Mo Kα radiation (0.7107 Å). A total of 2730 reflections was measured ($2\theta < 50°$), of which 2456 independent reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement. The intensities were corrected for Lorentz-polarization effects, and an absorption correction by the ψ scan method was applied. Crystal and experimental data: $a = 17.415(8)$, $b = 18.938(6)$, $c = 10.298(3)$ Å, $U = 3396$ Å^3, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $D_{calcd} = 1.400$ g cm^{-3}, $\mu = 5.74$ cm^{-1}, scan method ω–2θ, scan speed 16° min^{-1}, $T = 296$ K. The structure was solved by direct methods with MITHRIL (G.J. Gilmore, *J. Appl. Cryst., 17* (1984) 42). The coordinates of hydrogen atoms were calculated at ideal positions with the C–H distance of 0.95 Å and were not refined. Final full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms converged to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.038$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$) = 0.031. A final difference Fourier synthesis showed peaks at heights up to 0.33 e Å^{-3}. The absolute configuration was not determined. All calculations were carried out on a Digital VAX Station 3100 M38 with the TEXSAN-TEXRAY Program System.

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12 Complex **3** was prepared by the ligand exchange reaction of (η^6-C_6Me_6)Ru(η^1-C≡CPh)(2,6-$Me_2C_6H_3NC$)Cl with PPh_3. Details will be described in our subsequent report. Yield 42%. Calcd. for $C_{38}H_{38}RuPCl·0.25CH_2Cl_2$: C, 67.22; H, 5.68. Found: C, 67.40; H, 5.28%. IR (Nujol): ν(C≡C) 2091 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.80 (s, CH_3).

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