and thus we can have confidence in the static model charge densities. $N_{obs} =$ 11182 (only multiple measured reflections), $N_{par} = 1128$, GOF = 1.13, $R_{F2} =$ 0.035, $R_{wF2} = 0.046$.

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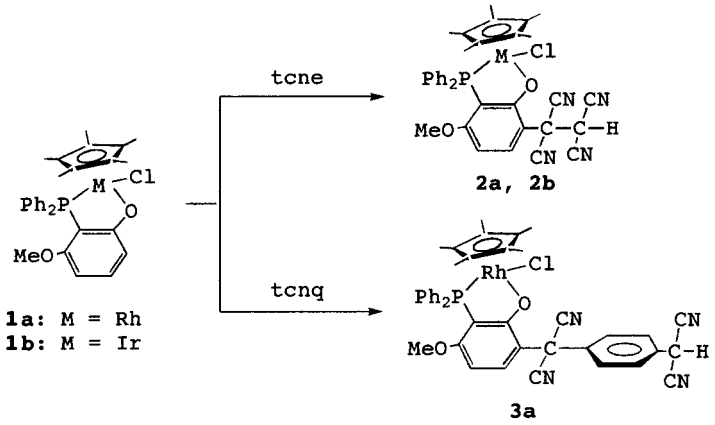
Pentamethylcyclopentadienylrhodium(III) and -iridium(III) Complexes Showing P,O Coordination: Unprecedented Insertion of tcne and tcnq into a C–H Bond**

Yasuhiro Yamamoto,* Xiao-Hong Han, Ken-ichiro Sugawara, and Saho Nishimura

Tetracyanoethylene (tcne) forms a variety of charge transfer and organometallic complexes as a result of its strong electrophilicity.[1] It is widely used as a precursor of organic magnets, the tetracyanoethylene-based organic magnets.[2] Reactions of tcne with metal – acetylide, metal – hydride, or metal – η^1-dienyl complexes exhibit characteristic features: 1) insertion into M–C bonds[3a, b] and into M–H bonds to afford cyano(dicyanomethyl)keteniminato complexes;[3c–e] 2) [2+2] addition to acetylide groups to give cyclobutene – metal complexes;[4] 3) [4+2] or [3+2] addition to diene moities to produce cyclohexene– or cyclopentane – metal complexes;[5] 4) α,β addition of dicyanomethylene fragments, derived from cleavage of the double bond of tcne, to an acetylide group.[6] In all cases except for (1), tcne is reactive to strongly activated unsaturated groups on the ligands.

Recently we reported that one of the *ortho*-methoxy groups in (2,6-dimethoxyphenyl)diphenylphosphane (MDMPP) is demethylated upon reaction with bis[dichloro(η^6-arene)ruthenium(II)] or bis[dichloro(η^5-pentamethylcyclopentadienyl)-rhodium(III)] to give [(η^6-arene)RuCl(MDMPP-*P,O*)][7a, b] and [(η^5-C_5Me_5)RhCl(MDMPP-*P,O*)],[8] respectively (MDMPP-*P,O* = PPh_2(2-O-6-MeO-C_6H_3), a P,O chelating phosphane). These complexes react with Lewis bases (L) in the presence of PF_6^- to give the corresponding cationic complexes [(η^6-arene)Ru(MDMPP-*P,O*)(L)][PF_6][7c] and [(η^5-C_5Me_5)Rh(MDMPP-*P,O*)(L)][PF_6].[8] While investigating the interactions of these complexes with small molecules such as olefins and alkynes, we found that tcne inserted into a weakly activated C–H bond on the substituted phenyl ring of the phosphane ligand upon reaction with the rhodium(III) or iridium(III) complexes [(η^5-C_5Me_5)MCl(MDMPP-*P,O*)] (**1a**: M = Rh,[8] **1b**: M = Ir[9]). This represents novel reactivity for tcne.

When tcne was added to **1a** or **1b** in CH_2Cl_2 at room temperature (Scheme 1), the solution became brown or yellow. In each case a 1:1 adduct was isolated, which on the basis of fast atom bombardment (FAB) mass spectrometry was assigned as **2a** (*m/z* 709 [M^+], orange-brown) or **2b** (*m/z* 798 [M^+], yellow; see the Experimental Section). In the IR spectrum of **2a** a very weak C≡N stretching frequency appeared at 2250 cm^{-1}, which is at higher energy than that of free tcne (2207 cm^{-1}) and π-complexed tcne (2170 – 2235 cm^{-1}).[1] However, no IR signal was observed for **2b** as bands in the ν_{CN} region are extremely weak. In the ^{1}H NMR spectra of **2** three characteristic resonances around $\delta = 1.50$,



Scheme 1. Reactions of complexes **1** with tcne or tcnq.

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3.50, and 6.40 were assigned to the η^5-C_5Me_5 (Cp*), methoxy, and $HC(CN)_2$ protons, respectively.

The structure of **2b** was determined by X-ray crystal structure analysis (Figure 1). The tcne molecule has been inserted into the C–H bond adjacent to the Ir–O σ bond. The

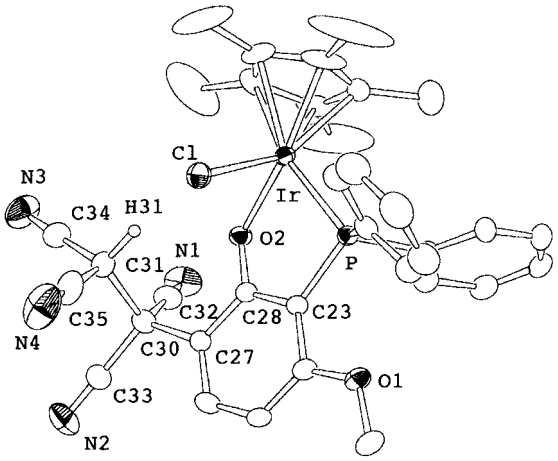

Figure 1. ORTEP diagram of the structure of **2b** with thermal ellipsoides drawn at the 30% probability level (see Table 1).

C30–C31 bond length of 1.592(7) Å is in the range of a usual C–C single bond (Table 1). The $CH(CN)_2$ and $C(CN)_2R$ groups adopt a staggered conformation (torsion angles C27-C30-C31-C34 168.8(5)°, C27-C30-C31-C35 −67.1(6)°). The Cl···H31 and Cl···C31 interatomic contacts are 2.78 and 3.63 Å, respectively, suggesting the presence of a very weak interaction.

Table 1. Selected bond lengths [Å] and angles [°] for **2b**.

Ir–Cl	2.411(2)	Ir–P	2.311(1)
Ir–O2	2.096(3)	O1–C24	1.352(6)
O2–C28	1.311(6)	C27–C30	1.517(7)
C30–C31	1.592(7)	C30–C32	1.494(8)
C32–N1	1.116(7)	C30–C33	1.489(8)
C33–N2	1.127(7)	C31–C34	1.452(8)
C34–N3	1.134(8)	C31–C35	1.450(9)
C35–N4	1.125(9)		
Cl-Ir-P	89.99(5)	Cl-Ir-O2	80.88(10)
P-Ir-O2	81.56(9)	Ir-P-C23	99.7(2)
Ir-O2-C28	117.9(3)	O2-C28-C23	122.3(4)
P-C23-C28	113.4(3)	C27-C30-C31	110.1(4)
C27-C30-C32	112.0(5)	C31-C30-C33	108.7(5)
C32-C30-C33	107.0(5)	C30-C31-C34	112.9(5)
C30-C31-C35	110.1(5)	C34-C31-C35	110.6(5)

These results prompted us to investigate the reaction with 7,7,8,8-tetracyano-*p*-quinodimethane (tcnq). Complex **1a** readily reacts with tcnq to form orange crystals formulated as the 1:1 adduct **3a** (Scheme 1), based on elemental analysis and FAB mass spectrometry (*m*/*z* 785 [M^+]; see the Experimental Section). The IR spectrum of **3a** showed a C≡N stretching frequency at 2247 cm^{-1}, which is about 20 cm^{-1} higher in energy than that for free tcnq. The ^1H NMR spectrum showed three characteristic resonances at $\delta = 1.35$ (d), 3.44 (s), and 5.08 (s), assignable to the Cp*, methoxy, and $HC(CN)_2$ protons, respectively. These chemical shifts appeared upfield in comparison with those for **2**; this is a result of the strong electron withdrawing ability of the $C(CN)_2$-$C(CN)_2$ moiety. The signal for the *para*-proton is an AB-type quartet, suggesting aromatization of the quinone group.

The crystal structure analysis of **3a** verified the conversion of the quinone ring into an aromatic ring upon insertion of tcnq into the C–H bond (Figure 2). The bulky $C_6H_4C(CN)_2H$

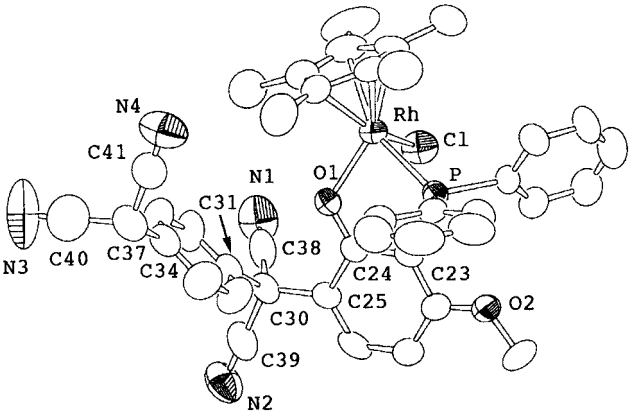

Figure 2. ORTEP diagram of the structure of **3a** with thermal ellipsoides drawn at the 50% probability level (see Table 2).

moiety is pointing in the opposite direction as the Cl ligand, relieving steric repulsion between the two groups. The C30–C31 and C34–C37 bond lengths are 1.54(1) and 1.56(1) Å, respectively, in agreement with a C–C single bond (Table 2). The $C30(CN)_2R$ and $C37(CN)_2H$ groups adopt a staggered conformation, similar to the case in **2a**.

Table 2. Selected bond lengths [Å] and angles [°] for **3a**.

Rh–Cl	2.393(2)	Rh–P	2.306(3)
Rh–O1	2.085(7)	C25–C30	1.54(1)
C30–C31	1.54(1)	C34–C37	1.56(2)
C30–C38	1.49(2)	C38–N1	1.18(2)
C30–C39	1.48(2)	C39–N2	1.14(1)
C37–C40	1.53(2)	C40–N3	1.12(2)
C7–C41	1.47(2)	C41–N4	1.13(2)
Cl-Rh-P	85.0(1)	Cl-Rh-O1	86.3(2)
P-Rh-O1	82.1(2)	Rh-P-C23	99.3(3)
Rh-O1-C24	118.5(6)	O1-C24-C23	122.3(9)
P-C23-C24	113.3(7)	C25-C30-C31	112.1(8)
C25-C30-C38	108.6(8)	C25-C30-C39	110.2(9)
C31-C30-C38	112.4(9)	C31-C30-C39	107.1(8)
C38-C30-C39	106.3(9)	C34-C37-C40	111(1)
C40-C37-C41	109(1)		

Complexes **1a** and **1b** were treated with moderately electron withdrawing olefins such as fumaronitrile and dimethyl fumarate in methanol at room temperature or at reflux. The starting materials were recovered quantitatively.

To our knowledge these results represent the first examples of insertion reactions of tcne and tcnq into a C–H bond on an aromatic ring. These reactions demonstrate the novel C–H bond activation by organometallic complexes in connection with insertion of strongly electron withdrawing cyanoolefins.

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Experimental Section

2a: To a solution of **1a** (53.2 mg, 0.092 mmol) in CH_2Cl_2 (10 mL) was added tcne (13 mg, 0.10 mmol) at room temperature. After 4 h the solvent was removed, and the solids were washed with diethyl ether. The residue was crystallized from CH_2Cl_2 and diethyl ether to give orange-brown crystals of **2a** (43.2 mg, 66.3 %). IR (nujol): $\tilde{\nu} = 2250\ cm^{-1}$ (C≡N); UV/Vis (CH_2Cl_2): $\lambda_{max} = 392$, 329 nm; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.50$ (d, $J(P,H) = 5.0$ Hz, Cp*), 3.48 (s, OMe), 5.27 (s, CH_2Cl_2), 6.36 (s, CH), ca. 6.06 and 7.3 – 8.0 (m, ArH); ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 45.2$ (d, $J(Rh,P) = 142.7$ Hz); FAB-MS: m/z: 709 [M^+], 673 [$M^+ - Cl$]; elemental analysis calcd for $C_{35}H_{31}N_4O_2PClRh \cdot CH_2Cl_2$: C 54.46, H 4.19, N 7.06; found: C 54.87, H 4.08, N 6.84.

2b: Yellow crystals of **2b** (41.4 mg, 42.9 %) were obtained from **1b** (80 mg, 0.121 mmol) and tcne (21.8 mg, 0.170 mmol) by a precedure similar to that for **2a**. UV/Vis (CH_2Cl_2): $\lambda_{max} = 324$ nm; ^1H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.53 (s, Cp*), 3.50 (s, OMe), 5.24 (s, CH_2Cl_2), 6.31 (s, $HC(CN)_2$), ca. 6.13 and 7.2 – 7.9 (m, ArH); ^{31}P NMR(100 MHz, $CDCl_3$): $\delta = 26.2$ (s); FAB-MS: m/z: 798 [M^+]; elemental analysis calcd for $C_{35}H_{31}N_4O_2PClIr$: C 52.66, H 3.91, N 7.02; found: C 52.98, H 3.84, N 7.00. Crystal data: $C_{35}H_{31}N_4O_2PClIr$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.123(5)$, $b = 14.314(7)$, $c =$ 20.407(3) Å, $\beta = 95.34(2)^\circ$, $V = 3525(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.504\ g\,cm^{-3}$, $R =$ 0.028 and $Rw = 0.037$ [$w = 1/\sigma^2(F_o)$] for 4487 reflections [$I > 3.0\sigma(I)$] with 397 variables. The structure was solved by Patterson methods (DIRDIF92) and refined by full-matrix least-squares techniques using the teXsan program package.[10]

3a: Orange crystals of **3a** (28 mg, 32 %) were obtained from **1a** (60 mg, 0.103 mmol) and tcnq (25 mg, 0.13 mol) by a precedure similar to that for **2a**. IR (nujol): $\tilde{\nu} = 2247\ cm^{-1}$ (C≡N); UV/Vis (CH_2Cl_2): $\lambda_{max} = 398$, 330 nm; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.35$ (d, $J(P,H) = 3.0$ Hz, Cp*), 3.44 (s, OMe), 5.08 (s, CH), 7.51 (AB q, $J = 10.0$ Hz), ca. 6.00 and 7.3 – 8.0 (m, ArH); ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 8.4$ (d, $J(Rh,P) = 150.0$ Hz); FAB-MS: m/z: 785 [M^+], 750 [$M^+ - Cl$]; elemental analysis calcd for $C_{41}H_{35}N_4O_2PClRh$: C 62.73, H 4.49, N 7.14; found: C 62.55, H 4.55, N 7.29. Crystal data: $C_{41}H_{35}N_4O_2PClRh$, monoclinic, space group $P2_1/n$ (no. 14), $a = 13.70(1)$, $b = 19.076(7)$, $c = 15.965(10)$ Å, $\beta = 101.31(6)^\circ$, $V = 4092(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.274\ g\,cm^{-3}$, $R = 0.055$ and $Rw = 0.080$ for 2961 reflections [$I >$ $4.0\sigma(I)$] with 451 variables. The structure was solved by Patterson methods (DIRDIF92) and refined by full-matrix least-squares techniques using the teXsan program package.[10]

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New Tripodal, "Supercharged" Analogues of Adenosine Nucleotides: Inhibitors for the Fhit Ap_3A Hydrolase**

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Diadenosine polyphosphates, discovered over 30 years ago,[1] are ubiquitous components of all cells. Recently, diadenosine triphosphate and tetraphosphate, Ap_3A and Ap_4A, have assumed vital significance as ligands for the tumor suppressor protein, Fhit,[2a] which is an Ap_3A hydrolase[2b] whose signalling appears to depend on Ap_nA binding.[3] We are interested in the specific enzymes of dinucleoside polyphosphate catabolism,[2a, 4, 5] in the chemistry[6] of those compounds, and also in bisubstrate analogues for phosphoglycerate[7] and other kinases, and present here the synthesis

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