Organopalladium and Platinum Complexes of C_{60} Bearing Isonitrile Ligands

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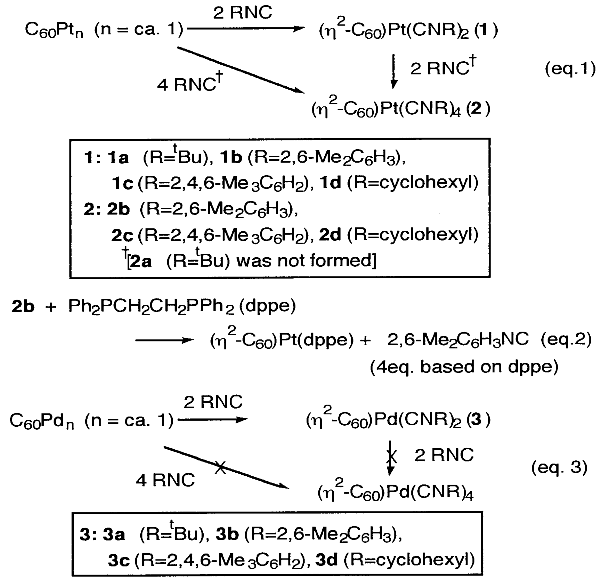
Organopalladium or platinum complexes, $(\eta^2\text{-}C_{60})M(CNR)_2$ (**1** M =Pt, **3**; M = Pd: R = ^{t}Bu, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, cyclohexyl) were synthesized from $C_{60}M_n$ (M = Pd, Pt; n = ca.1) and the corresponding isonitriles. Unprecedented reaction of **1** with additional isonitriles occurred to form $(\eta^2\text{-}C_{60})Pt(CNR)_4$ (**2**) in the case where R = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, cyclohexyl).

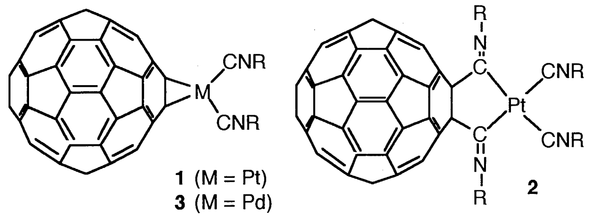
Organometallic compounds of fullerenes have contributed to understanding the structure and chemical nature of these.[1] Despite their potential reactivity, these complexes are generally stable, and do not react with organic substrates. In the famous Fagan complex $(\eta^2\text{-}C_{60})Pt(phosphines)_2$, C_{60} acts like an electron-deficient olefin and bonds with electron-donating metal fragments.[1a,1b] Theoretical studies suggested that large back-donation from the metal fragment to LUMO of the C_{60} moiety was important to stabilize the complex.[2] Our interest has been focussed on the introduction of less electron-donating organoplatinum fragments than $Pt(phosphine)_2$ to C_{60}, in which insufficient back-donation from the metal fragment may result in destabilization of the complexes and lead to their new reactivity. We wish to report here that such organoplatinum complexes, $(\eta^2\text{-}C_{60})Pt(CNR)_2$ (**1**), are easily synthesized from $C_{60}Pt_n$ (n = ca.1)[3a] and isonitriles. Homologous organopalladium complexes (**3**) were also prepared from $C_{60}Pd_n$ (n = ca. 1).[3b] Of importance is that the platinum complexes **1** unprecedentedly reacted with additional isonitriles to form $(\eta^2\text{-}C_{60})Pt(CNR)_4$ (**2**).

As described earlier, $C_{60}Pt_n$ (n = ca. 1) reacted with phosphines and phosphites to give $(\eta^2\text{-}C_{60})PtL_2$ [L = PR_3, $P(OR)_3$].[3] By using a similar procedure, the isonitrile complexes **1** were prepared by the reaction of $C_{60}Pt_n$ (n = ca.1) with isonitriles. In a typical example, treatment of $C_{60}Pt_n$ with CN^{t}Bu (2 eq.) in toluene at room temperature for 3 h afforded $(\eta^2\text{-}C_{60})Pt(CN^tBu)_2$ (**1a**) in 93% yield.[4] ^{13}C NMR resonances assigned to the C_{60} ligand were similar to those of $(\eta^2\text{-}C_{60})Pt(phosphines)_2$;[1a, 1b, 3] this indicates that the structure of **1a** is similar to the Fagan complex. Three reversible reduction waves observed for **1a**,[4] of which reduction potentials were more negative than those of C_{60} but more positive than those of $(\eta^2\text{-}C_{60})Pt(phosphines)_2$,[5] clearly revealed that the $Pt(CN^tBu)_2$ species was a poorer electron-donor than the $Pt(phosphine)_2$ fragment.

Unprecedented reaction was discovered in the experiments to synthesize $(\eta^2\text{-}C_{60})Pt[CN(2,6\text{-}Me_2C_6H_3)]_2$ (**1b**). Careful treatment of $C_{60}Pt_n$ (n = ca.1) with CN(2,6-$Me_2C_6H_3$) (2 eq.) resulted in successful synthesis of **1b** in 72% yield with spectroscopic data similar to those of **1a**. However, this compound was readily reacted with additional isonitriles to form a new complex of which the formula is $(\eta^2\text{-}C_{60})Pt[CN(2,6\text{-}Me_2C_6H_3)]_4$ (**2b**) in 77% yield. Synthesis of **2b** was alternatively achieved by treatment of $C_{60}Pt_n$ (n = ca.1) with 4 equivalents of 2,6-$Me_2C_6H_3NC$ in 72% yield. The formula of **2b** was evidenced by the fact that the molecular ion peak (M = 1439) was observed in the FAB-mass spectrum which had isotope intensities consistent with those of calculated values. The following quantitative experiments using ^1H NMR spectra also supported the formula of **2b**; exactly two equivalents of CN(2,6-$Me_2C_6H_3$) reacted with **1b** to form **2b**, whereas the reaction of **2b** with 1 eq. of dppe ($Ph_2PCH_2CH_2PPh_2$) gave $(\eta^2\text{-}C_{60})Pt(dppe)$ with exactly 4 eq. of CN(2,6-$Me_2C_6H_3$) based on **2b** (Scheme 1, eq.2).



Scheme 1.



1 (M = Pt)
3 (M = Pd)
2

Figure 1.

Spectroscopic data of **2b** indicated that two different types of isonitrile ligands were bonded to platinum. IR spectrum of **2b** showed three vibrations at 2179, 2156, and 1608 cm^{-1}. Two sets of resonances derived from the 2,6-$Me_2C_6H_3$ group were observed both in ^1H and ^{13}C NMR. One set of proton signals was apparently shifted upfield (~1ppm). Carbon resonances derived from C_{60} consisting of 17 signals are indicative of the existence of C_{2v} symmetry in the molecule. It is noteworthy that one peak appeared at a higher field (δ 89.2 ppm) than the others. ^{13}C Resonances in this region are characteristic for sp^3-like carbons in the C_{60} moiety, which are bonded to organic fragments in organofullerene derivatives.[6] Although carbon signals of CNAr were difficult to observe in the ^{13}C NMR of **2b**, they were observed in that of $(\eta^2\text{-}C_{60})Pt[^{13}CN(2,6\text{-}Me_2C_6H_3)]_4$ (**2b***) prepared from $C_{60}Pt_n$ (n = ca.1) and $^{13}CN(2,6\text{-}Me_2C_6H_3)$; two signals derived from the quaternary carbons of isonitriles appeared at δ 144.4 and 196.1 ppm. Each of them was accompanied by a satellite due to the coupling with ^{195}Pt ($^1J_{Pt\text{-}C}$ = 960 and 1090 Hz, respectively). Each peak split into a doublet presumably due to the ^2J coupling with the other coordinated ^{13}CNR. Although unequivocal elucidation of the structure should be awaited for X-ray analysis, we tentatively propose the structure **2b** containing both "terminal" and "bridging" isonitrile ligands (R = 2,6-Me_2CH_3NC in Figure 1) from the above spectroscopic data, which was formed by insertion of two isonitriles between carbon-platinum bonds in **1b**.

Experiments to synthesize similar platinum complexes with different isonitriles and analogous palladium complexes revealed the following: The reactivity of the insertion reaction was dependent on the structure of isonitriles; the t-butylisonitrile complex **1a** did not react with additional ^tBuNC even at higher temperature (~110 °C in toluene-d_8), whereas two other isonitrile complexes, $(\eta^2\text{-}C_{60})Pt[CN(2,4,6\text{-}Me_3C_6H_2)]_2$ (**1c**) and $(\eta^2\text{-}C_{60})Pt[CN(cyclohexyl)]_2$ (**1d**) easily reacted with excess isonitriles to form $(\eta^2\text{-}C_{60})Pt[CN(2,4,6\text{-}Me_3C_6H_2)]_4$ (**2c**) and $(\eta^2\text{-}C_{60})Pt[CN(cyclohexyl)]_4$ (**2d**), respectively. Steric bulkiness of the t-butyl group presumably prevented the migratory insertion. The palladium complexes $(\eta^2\text{-}C_{60})Pd(CNR)_2$ (**3**) were successfully prepared by the reaction of $C_{60}Pd_n$ (n = ca.1) with isonitriles (^tBuNC, 2,6-$Me_2C_6H_3NC$, 2,4,6-$Me_3C_6H_2NC$, and cyclohexylNC) (Scheme 1, eq.3); however, they did not react with excess isonitriles to form $(\eta^2\text{-}C_{60})Pd(CNR)_4$ even at higher temperatures.

All of these results are interesting in comparison with well investigated chemistry of the transition metal complexes bearing isonitrile ligands.[9] In isonitrile complexes $(\eta^2\text{-alkene})M(CNR)_2$ synthesized by Otsuka (M = Ni, Pd) and Stone (M = Pt), electron-deficient alkenes such as TCNE and maleic anhydride effectively stabilize these complexes to compensate a good σ-donor character of isonitriles.[9] Since C_{60} is an electron acceptor comparable to TCNE, it is reasonable to form stable $(\eta^2\text{-}C_{60})M(CNR)_2$ (M = Pd, Pt). It is noteworthy that the reaction of $(\eta^2\text{-alkene})M(CNR)_2$ with isonitriles to form $(\eta^2\text{-alkene})M(CNR)_4$ has not yet been reported. Furthermore, the insertion was observed only in the platinum complexes and not in the palladium complexes; this is inconsistent with a general trend that the isonitrile insertion into palladium alkyls often occurs more readily than into platinum alkyls. In contrast to the fact that multiple insertion readily occurs into metal-alkyl bonds in usual isonitrile complexes, only two molecules of isonitriles were inserted to the metal-alkyl bonds in $(\eta^2\text{-}C_{60})Pt(CNR)_2$. The "bridging" isonitriles are not very stable and their facile liberation from the coordination sphere was seen in the reaction of dppe with $(\eta^2\text{-}C_{60})Pt(CNR)_4$. These features have not been observed in known chemistry of transition metal complexes bearing isonitriles, and may be affected by the special nature of the C_{60} ligands. We are now actively investigating the mechanisms of this insertion reaction in comparison with $(\eta^2\text{-}C_{60})M(CNR)_2$ (M = Pd, Pt).

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References and Notes

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4 **1a**: IR (KBr) 2140. ^1H NMR (C_6D_6) δ 0.86 (s). ^{13}C NMR ($CDCl_3$ at -30°C) δ 30.2, 57.7, 135.0, 149.0, 141.5, 141.9, 142.0, 142.8, 142.9, 143.0, 143.2, 143.7, 144.0, 144.1, 144.4, 145.3, 146.1, 147.2, 157.8. CV; -1.09, -1.69, -2.25 V vs Fc/Fc^+; **1a** (0.2 mM) and $TBAPF_6$ (0.2 mM) in THF at -78°C; Pt electrode. Peaks derived from dissociated C_{60} were also visible.[5]

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6 **2b**: ^1H NMR ($CDCl_3$) δ 2.21 (s, 12H, Me), 2.34 (s, 12H, Me), 6.38 (t, 2H, J = 8.0 Hz), 6.70 (d, 4H, J = 8.0 Hz), 7.02 (d, 4H, J = 8.0 Hz), 7.18 (t, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ R in the isonitrile ligands; 18.4, 19.7, 122.4, 127.1, 126.7 (2C), 127.7, 129.3, 134.4, 134.7. the C_{60} moiety; 89.2, 139.9, 141.6, 142.3, 142.4, 142.5, 142.7, 144.5, 144.9, 145.1, 145.8, 145.9, 146.0, 147.2, 148.2, 153.3, 157.4.

7 For example, H. Nagashima, H. Terasaki, E. Kimura, K. Nakajima, and K. Itoh, *J. Org. Chem.* **59**, 1246 (1994).

8 Other supporting evidence for the existence of both terminal and bridging isonitriles was obtained in ^1H NMR of **2b** in the presence of excess $CN(2,6\text{-}Me_2C_6H_3)$, in which only one set of coordinated isonitrile protons (Me δ 2.21) was broadened with remaining the other (Me δ 2.34) intact. This indicates exchange of only terminal isonitriles with uncoordinated isonitriles in NMR time scale.

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