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# Structural Versatility of 5-Methyltetrazolato Complexes of ($\eta^5$-Pentamethylcyclopentadienyl)iridium(III) Incorporating 2,2′-Bipyridine, *N*,*N*-Dimethyldithiocarbamate, or 2-Pyridinethiolate Ligands

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Several new mono- and dinuclear $\eta^5$-pentamethylcyclopentadienyl (Cp*) iridium(III) complexes bearing 5-methyltetrazolate ($MeCN_4^-$) have been synthesized and their molecular and crystal structures have been determined. For complexes incorporating 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), both mononuclear $\kappa N^2$-coordinated and dinuclear $\mu$-$\kappa N^1$:$\kappa N^3$-bridging $MeCN_4$ complexes were obtained: $[Cp^*Ir(bpy\ or\ phen)(MeCN_4\text{-}\kappa N^2)]PF_6$ (**1** or **3**) and $[\{Cp^*Ir(bpy\ or\ phen)\}_2(\mu\text{-}MeCN_4\text{-}\kappa N^1{:}\kappa N^3)](PF_6)_3$ (**2** or **4**), respectively. It was confirmed by X-ray analysis that the dinuclear complex in **2** has a characteristic structure with a pyramidal pocket constructed from a $\mu$-$\kappa N^1$:$\kappa N^3$-bridging $MeCN_4^-$ and two bpy ligands. In the case of analogous complexes with *N*,*N*-dimethyldithiocarbamate ($Me_2dtc^-$), yellow platelet crystals of mononuclear $\kappa N^1$-coordinated complex, $[Cp^*Ir(Me_2dtc)(MeCN_4\text{-}\kappa N^1)] \cdot HN_4CMe$ ($\mathbf{5} \cdot HN_4CMe$), and yellow prismatic crystals of dinuclear $\mu$-$\kappa N^1$:$\kappa N^4$-bridging one, $[\{Cp^*Ir(Me_2dtc)\}_2(\mu\text{-}MeCN_4\text{-}\kappa N^1{:}\kappa N^4)]PF_6$ (**6**), were deposited. The $\kappa N^1$- and $\kappa N^1$:$\kappa N^4$-bonding modes of $MeCN_4^-$ in these complexes presumably arise from the compactness of the $Me_2dtc^-$ coligand. **6** is the first example in which tetrazolates act as a $\mu$-$\kappa N^1$:$\kappa N^4$-bridging ligand. Furthermore, the molecular and crystal structures of dinuclear complexes having $\mu$-$\kappa^2 S,N{:}\kappa S$-bridging 2-pyridinethiolate (2-Spy$^-$) or 8-quinolinethiolate (8-Sqn$^-$) ligands have been determined: $[(Cp^*Ir)_2(\mu\text{-}2\text{-}Spy\ or\ 8\text{-}Sqn\text{-}\kappa^2 S,N{:}\kappa S)_2]$ (**7** or **8**). These thiolato-bridging complexes were stable toward the addition of 5-methyltetrazole ($HN_4CMe$), owing to the characteristic intramolecular stacking interaction between the pyridine or the quinoline rings. The 2-Spy complex of **7**, however, reacted with an excess amount of $Na(N_4CMe)$, resulting in cleavage of the Ir—N(py) bond and coordination of $MeCN_4^-$ in the $\mu$-$\kappa N^2$:$\kappa N^3$-bridging mode: $[(Cp^*Ir)_2(\mu\text{-}2\text{-}Spy\text{-}\kappa S{:}\kappa S)_2(\mu\text{-}MeCN_4\text{-}\kappa N^2{:}\kappa N^3)]PF_6$ (**9**). This bridging mode of $MeCN_4^-$ was also observed in the triply bridging $MeCN_4$ complex: $[(Cp^*Ir)_2(\mu\text{-}MeCN_4\text{-}\kappa N^2{:}\kappa N^3)_3]PF_6$ (**10**). In these various $MeCN_4$ complexes, the structural parameters of the $MeCN_4$ moiety were not perturbed by the difference in the bonding modes.

## Introduction

In the design and construction of metallo-organic hybrid materials, one of the most important concepts is the spatial control of the molecular building blocks.[1–6] For versatile bridging ligands having multiple coordination modes, it is particularly significant to elucidate the factors that control their bonding patterns.[6–9] One class of such versatile bridging

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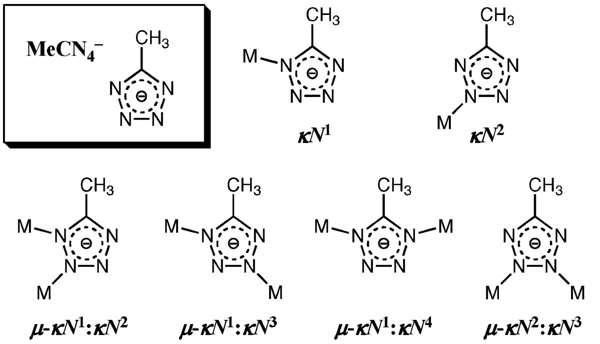
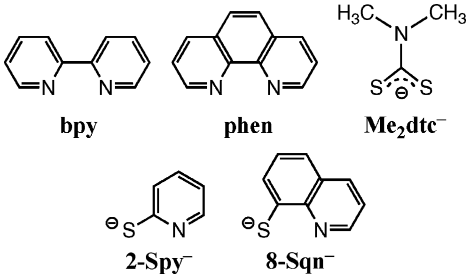
**Scheme 1.** 5-Methyltetrazolate (MeCN$_4^-$) and Its Coordination and Bridging Modes in Mono- and Dinuclear Complexes



**Scheme 2.** Various Bidentate Coligands Used in This Study



ligands is tetrazolates (RCN$_4^-$), which have four possibly ligating nitrogen atoms in a heteroaromatic five-membered ring. Tetrazolates form two possible linkage isomers when they act as a monodentate ligand and also have four possible bridging modes if they bind two metal centers (Scheme 1). Thus, the diversity of the coordination modes of tetrazolates is prominent as compared to those of other nitrogen-containing heteroaromatic compounds, such as triazolates, pyrazolates, and imidazolates. However, because the basicity of their nitrogen sites becomes weaker as the number of the nitrogen atoms in the ring increases,[10,11] the coordination ability of tetrazolates is expected to be rather weak. This may be one of the reasons why studies on tetrazolato complexes are limited.[12–22] Most of the previous studies were focused on the formation of tetrazolates by the 1,3-dipolar cycloaddition reaction of an azide ion (or ligand) and a nitrile on a metal center[12–15] and on the linkage isomerism of the monodentate coordination compounds.[13,15,18] There were only a few papers concerning dinuclear complexes bridged by tetrazolates,[16,17] and to our best knowledge, no reports have been published on dinuclear complexes having 5-methyltetrazolate as a bridging ligand.

In this study, we have prepared various types of MeCN$_4$ complexes using Cp*Ir$^{\text{III}}$(L—L) fragments (Cp* = $\eta^5$-C$_5$Me$_5$; L—L = bidentate ligands listed in Scheme 2). We also reveal the dependence of the selectivity of coordination and bridging modes of MeCN$_4^-$ in mono- and dinuclear complexes on the coligand L—L.

## Results and Discussion

**5-Methyltetrazolato Complexes Incorporating 2,2′-Bipyridine.** A yellow methanol solution was prepared by a reaction of [Cp*IrCl(bpy)]Cl and AgOTf (TfO$^-$ = CF$_3$SO$_3^-$) in a 1:2 molar ratio in methanol, followed by filtration of the resulting white precipitate (AgCl). Then, the solution was reacted with an equimolar mixture of 5-methyltetrazole (HN$_4$CMe) and sodium methoxide (NaOMe) in methanol, affording two kinds of Cp*Ir$^{\text{III}}$(bpy) complexes bearing MeCN$_4^-$ (eq 1). The $^1$H NMR spectrum of the reaction mixture (in CD$_3$CN) gave a singlet resonance at $\delta$ 1.60 due to the Cp* group of one product and two singlet resonances at $\delta$ 1.31 and 1.44 due to the nonequivalent Cp* groups of the other. The formation ratio of the two products was approximately 3:2, and each one could be obtained selectively when the reaction conditions were optimized. The former complex exhibiting a single Cp* resonance was obtained nearly quantitatively when an excess (more than quintuple the molar quantity) of Na(N$_4$CMe) was applied in the reaction and could be isolated as the PF$_6$ salt, [Cp*Ir(bpy)(MeCN$_4$)]PF$_6$ (**1**). The crystal structure of **1** was determined by X-ray analysis, which revealed the monodentate $\kappa N^2$-coordination mode of MeCN$_4^-$ (Figure 1). It is

$$[\mathrm{Cp^*IrCl(bpy)}]\mathrm{Cl}\ \xrightarrow[-\,2\ \mathrm{AgCl}]{+\,2\ \mathrm{Ag}^+}\ \xrightarrow{+\ \mathrm{MeCN_4}^-}\ \begin{array}{c}[\mathrm{Cp^*Ir(bpy)(MeCN_4)}]^+\ (\mathbf{1})\\ +\\ [\{\mathrm{Cp^*Ir(bpy)}\}_2(\mathrm{MeCN_4})]^{3+}\ (\mathbf{2})\end{array} \qquad (1)$$

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known for 5-methyltetrazolate that the basicity at the $N^1$ site is higher than that at the $N^2$ site.[18b] On the other hand, because coordination through the $N^1$ atom directs the ortho-positioned methyl group toward the bpy coligand, it would be unfavorable from the steric point of view. For the Cp*Ir$^{\mathrm{III}}$(bpy) fragment, however, the $\kappa N^1$-coordination mode of $\mathrm{MeCN_4^-}$ is not impossible (in fact, the $\kappa N^1$-bonding mode was found in the dinuclear complex described below). The selective formation of **1** indicates the importance of steric congestion for the coordination of $\mathrm{MeCN_4^-}$. The structural parameters in the Cp*Ir$^{\mathrm{III}}$(bpy) fragment are normal as compared to those in [Cp*Ir($N_3$)(bpy)]$PF_6$[23] and other related [Cp*IrX(bpy)]$^{n+}$-type complexes.[24] The Ir—N($N_4$CMe) bond length is Ir1—N2 2.075(4) Å, which is comparable to the Ir—N(pz) length in [Cp*Ir(HBpz$_3$-$\kappa^2 N,N'$)Cl], 2.080(2) Å.[25]

The $^1$H NMR spectrum of **1** in $CD_3CN$ indicated that the $\kappa N^2$-coordinated complex exists in solution without any linkage isomerism; if $\mathrm{MeCN_4^-}$ was bound to the Ir$^{\mathrm{III}}$ center through the $N^1$ atom, the *Me*$\mathrm{CN_4^-}$ resonance would show a remarkably higher-field shift, owing to the ring current effect of the bpy group. The stability of the $\kappa N^2$-coordination mode in **1** is in contrast to the Pd$^{\mathrm{II}}$, Pt$^{\mathrm{II}}$,[13a,b,18a] and Co$^{\mathrm{III}}$[15,18b] complexes, where the $MeCN_4$ complexes exist as an equilibrium mixture of the $\kappa N^1$- and $\kappa N^2$-coordinated complexes in solution.

The other $MeCN_4$ complex (in eq 1), that showed two Cp* resonances at $\delta$ 1.31 and 1.44 with equal intensities, was solely synthesized by the reaction with an equimolar quantity of 5-methyltetrazole ($HN_4CMe$) and isolated as the $PF_6$ salt. The single-crystal X-ray analysis of the product confirmed the dinuclear structure of the tricationic complex, in which $\mathrm{MeCN_4^-}$ bridged unsymmetrically two iridium centers through the $N^1$ and $N^3$ atoms: [{Cp*Ir(bpy)}$_2$($\mu$-MeCN$_4$-$\kappa N^1$:$\kappa N^3$)]($PF_6$)$_3$·2$H_2O$ (**2**·2$H_2O$) (Figure 2). This dinuclear complex has a characteristic structure with a pyramidal pocket constructed from a $\mu$-$\kappa N^1$:$\kappa N^3$ bridging $\mathrm{MeCN_4^-}$ and two bpy planes (part *b* of Figure 2). This structure and configuration can reduce the steric congestion most effectively when the mononuclear complex **1** attaches another Cp*Ir(bpy) fragment. The Ir—N(bpy) bond lengths in **2**, 2.093(4)–2.094(4) Å, are comparable to those in **1**. However, the Ir2—N3 bond, 2.092(3) Å, is slightly longer than the corresponding Ir—N($MeCN_4$) bond in **1**, 2.075(4) Å, and the Ir1—N1 bond in **2**, 2.108(4) Å, is further longer. This elongation of the Ir1—N1 bond should be related to the steric repulsion of the ortho-positioned Me group of $\mathrm{MeCN_4^-}$ with the bpy coligand. Such a steric interaction also affects the coordination bond angles around the nitrogen atoms; whereas the angles of Ir2—N3—N2 and Ir2—N3—N4 are nearly the same as each other {123.1(3) vs 124.8(3)°}, the angle of Ir1—N1—C5 135.9(3)° is remarkably enlarged as compared to that of Ir1—N1—N2 115.3(3)°.

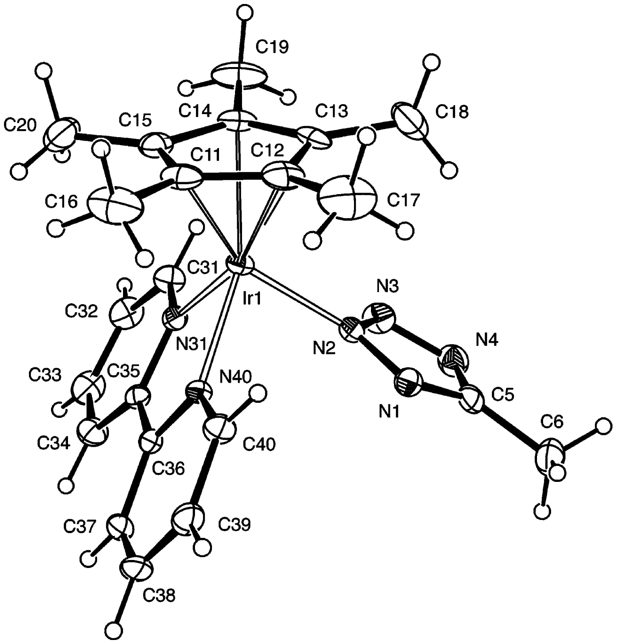

**Figure 1.** ORTEP (30% probability level) of the cation in [Cp*Ir(bpy)-($MeCN_4$-$\kappa N^2$)]$PF_6$ (**1**).

The $^1$H NMR spectrum indicated that the unsymmetrically $MeCN_4$-bridged dinuclear structure in **2** was maintained in $CD_3CN$ solution. Two nonequivalent Cp* resonances were diagnostically high-field shifted, as compared to those in **1** and other six-coordinated [Cp*Ir$^{\mathrm{III}}$X(L—L)]$^{n+}$-type complexes.[23,24] The *Me*$\mathrm{CN_4^-}$ resonance of **2** ($\delta$ 1.85) was also higher-field shifted than that of **1** ($\delta$ 2.13). The reactions of the bpy precursor complex with $HN_4CMe$ or Na($N_4$CMe) are collected in Scheme 3.

**Cycloaddition Reactions To Give the $MeCN_4$ Complexes.** It has been well documented that tetrazolato complexes are prepared by cycloaddition reactions of azido complexes with organic nitriles[12,13] or nitrile complexes with an azide anion.[12,15] Therefore, it is interesting to investigate in this study whether **1** and **2** are able to be synthesized by such cycloaddition reactions.

The azido complex, [Cp*Ir($N_3$)(bpy)]$PF_6$,[23] was stable in $CD_3CN$ (in the dark) at ambient temperature for several days. On heating the solution to 70 °C, however, a gradual formation of [Cp*Ir(bpy)($CD_3CN_4$-$\kappa N^2$)]$^+$ was detected by $^1$H NMR spectroscopy (the yield was 31% after 24 h). In this reaction, the formation of the other linkage isomer (i.e., the $\kappa N^1$-coordinated $CD_3CN_4$ complex) was not observed. Here, it should be noted that Purcell et al. studied the isomerization reaction of the $\kappa N^1$-bonded $MeCN_4$ complex of [Co($MeCN_4$-$\kappa N^1$)($NH_3$)$_5$]$^{2+}$, which was kinetically obtained by a reaction of [Co($NH_3$)$_5$($CH_3CN$)]$^{3+}$ and $\mathrm{N_3^-}$, to the thermodynamically more-stable $\kappa N^2$ isomer.[15] Hence, we thought that a reaction of an acetonitrile complex of Cp*Ir$^{\mathrm{III}}$(bpy) with the azide anion might give the $\kappa N^1$ isomer of **1**. The complex of [Cp*Ir(bpy)($CH_3CN$)]($PF_6$)$_2$ was obtained as a pale-yellow powdery compound by a reaction of [Cp*IrCl(bpy)]Cl with double the molar quantity of AgOTf, followed by removal of the white precipitate of AgCl and the addition of excess $NH_4PF_6$. A stoichiometric amount

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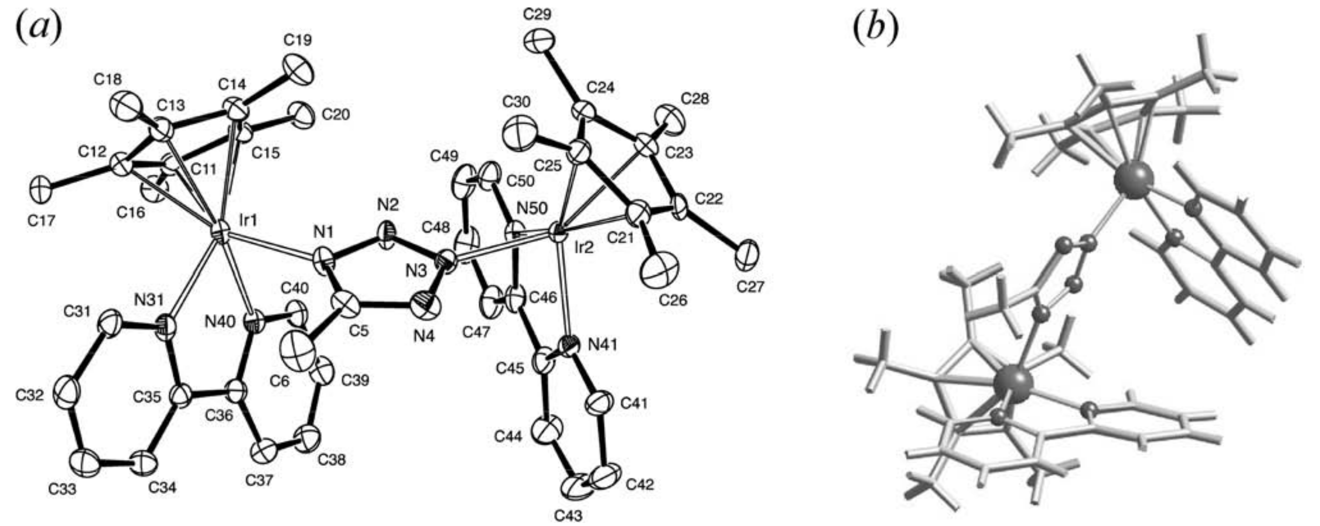
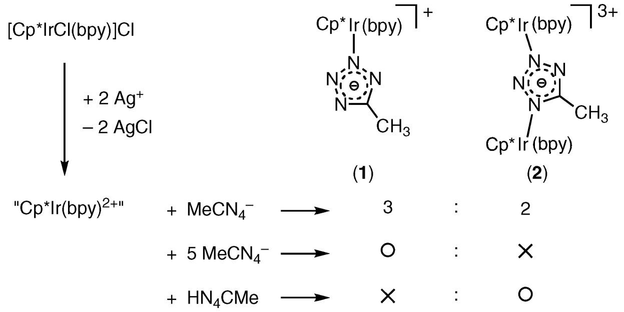
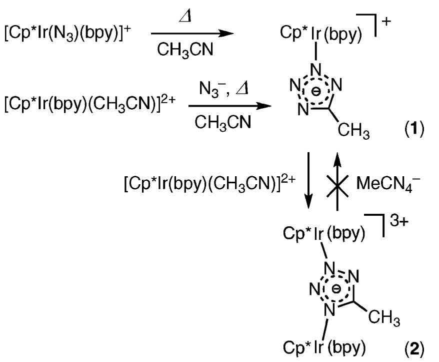


**Figure 2.** (*a*) ORTEP (30% probability level, hyrdogen atoms omitted) and (*b*) a schematic top view (iridium atoms are drawn as a large ball; nitrogen atoms as a small ball; carbon and hydrogen atoms as a stick) of the cation in [{Cp*Ir(bpy)}$_2$($\mu$-MeCN$_4$-$\kappa N^1$,$\kappa N^3$)](PF$_6$)$_3$·2H$_2$O (**2**·2H$_2$O).

**Scheme 3.** Reactions of the bpy Precursor Complex with 5-Methyltetrazole (HN$_4$CMe) or 5-Methyltetrazolate (MeCN$_4$$^-$)



**Scheme 4.** Cycloaddition Reactions To Give Cp*Ir(bpy)—MeCN$_4$ Complexes



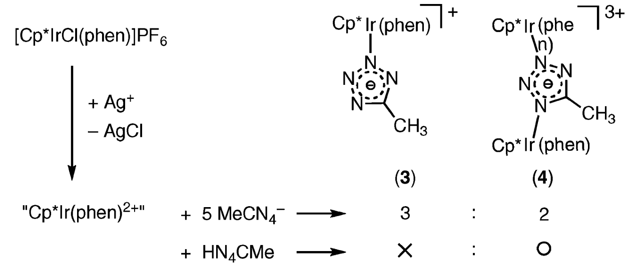
of NaN$_3$ (solid) was added to an acetonitrile-$d_3$ solution of [Cp*Ir(bpy)(CH$_3$CN)](PF$_6$)$_2$, and the thermal reaction of the mixture was monitored by $^1$H NMR spectroscopy. At the beginning, a small amount of the $N^2$-bonded MeCN$_4$ complex (**1**) was formed, but it was converted to the $\mu$-$\kappa N^1$:$\kappa N^3$-bridging dinuclear complex (**2**). After the reaction was completed, **2** was the sole product in the reaction. In a separate experiment, it was found that the addition of [Cp*Ir(bpy)(CH$_3$CN)](PF$_6$)$_2$ to an acetonitrile solution of **1** transformed quantitatively to the dinuclear complex **2**. These facts suggest that dinuclear complex formation is preferable rather than the cycloaddition reaction forming the 5-methyltetrazolato complex. On the other hand, even when an excess amount of Na(N$_4$CMe) was added to an acetonitrile solution of **2**, the mononuclear complex **1** could not be formed. This means that once the dinuclear complex is formed, it is substitution inert and kinetically very stable (Scheme 4).

**1,10-Phenanthroline Complexes.** With an analogous starting complex incorporating 1,10-phenanthroline (phen), [Cp*IrCl(phen)]PF$_6$, similar reactions to give the MeCN$_4$ complexes were examined. Likewise to the bpy complexes (Scheme 3), both mononuclear and dinuclear complexes, [Cp*Ir(phen)(MeCN$_4$)]PF$_6$ (**3**) and [{Cp*Ir(phen)}$_2$($\mu$-MeCN$_4$)](PF$_6$)$_3$ (**4**), were obtained. The mononuclear complex of **3** was expected to have the $\kappa N^2$-coordinated MeCN$_4$$^-$ due to the steric requirement from the Me group at 5-position (vide infra), although the crystal structure was not determined by X-ray analysis. The $^1$H NMR spectrum of **3** in CD$_3$CN showed the single Cp* and *Me*CN$_4$ resonances at $\delta$ 1.67 and 2.02, respectively, in the integration ratio of 5:1. This spectrum was stable for prolonged standing in the dark at ambient temperature, suggesting that neither the linkage isomerization of coordinated MeCN$_4$$^-$ nor the dinuclear complex formation to give a MeCN$_4$-bridged complex occurred under this condition. The cycloaddition reaction of CD$_3$CN to the azido complex of [Cp*Ir(N$_3$)(phen)]PF$_6$ under refluxing conditions was also detected by $^1$H NMR spectroscopy, which afforded [Cp*Ir(phen)(CD$_3$CN$_4$)]$^+$. The yield of the 5-methyltetrazolate complex was ca. 33%, after the reaction was performed at 100 °C for 13.5 h.

The dinuclear complex **4** was the sole product if the stoichiometric amount of HN$_4$CMe was applied in the reaction (Scheme 5). The $^1$H NMR spectrum of **4** showed two nonequivalent Cp* resonances at $\delta$ 1.26 and 1.46 and a *Me*CN$_4$ resonance at $\delta$ 1.73, all of which were relatively higher-field shifted than those of **3**. Therefore, the complex cation in **4** is reasonably assigned as a $\mu$-$\kappa N^1$:$\kappa N^3$-bridging dinuclear MeCN$_4$ structure, similar to the bpy complex **2**.

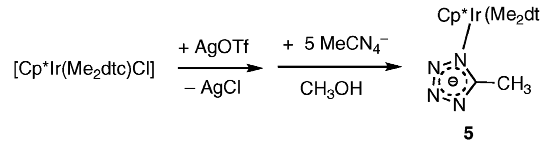
The overall reactions investigated with the phen precursor complex are very similar to those with the analogous bpy complex. One minor difference is the formation ratio of the

**Scheme 5.** Reactions of the phen Precursor Complex with 5-Methyltetrazolate ($MeCN_4^-$) or 5-Methyltetrazole ($HN_4CMe$)



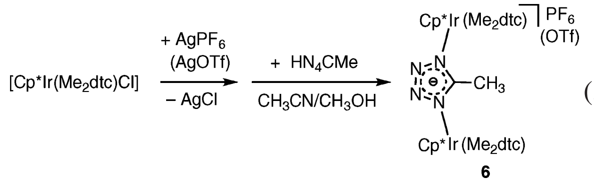
mono- and dinuclear complexes, **3** and **4**, as compared to the ratio of **1** and **2** under the same conditions. For example, when quintuple the molar quantity of $Na(N_4CMe)$ was applied in the reaction with $Cp^*Ir(phen)^{2+}$ (Scheme 5), both mono- and dinuclear products (**3** and **4**) resulted in the ratio of 3:2, whereas only the mononuclear complex **1** was obtained in the case of the bpy complex under the same reaction condition (Scheme 3).

**Syntheses and Structures of $MeCN_4$ Complexes Incorporating *N*,*N*-Dimethyldithiocarbamate.** With similar reaction conditions to the above bpy and phen complexes, the preparation of the corresponding complexes with *N*,*N*-dimethyldithiocarbamate ($Me_2dtc^-$) was attempted, using $[Cp^*Ir(Me_2dtc)Cl]$[26] as the starting complex. When an excess amount of $Na(N_4CMe)$ was applied (eq 2), the mononuclear complex $[Cp^*Ir(Me_2dtc)(MeCN_4)]$ (**5**) was produced. This complex was cocrystallized with free $HN_4CMe$: $[Cp^*Ir(Me_2dtc)(MeCN_4)]\cdot HN_4CMe$ (**5**·$HN_4CMe$) (Figure 3), as revealed by elemental analysis, spectroscopic measurements, and X-ray crystallography. The $HN_4CMe$ molecule in the crystal was hydrogen-bonded to the coordinated $MeCN_4^-$ ligand through the $N^1$—H moiety, N6(—H)···N4 2.737(7) Å, and also showed stacking interactions with the Cp* ring and another $HN_4CMe$ ring of the neighboring molecules (part *b* of Figure 3). The most striking feature in the molecular structure of **5**·$HN_4CMe$ is the $\kappa N^1$-coordination mode of $MeCN_4^-$. Because the basicity of the $N^1$-position of $MeCN_4^-$ is higher than that of the $N^2$-position,[18b] the $\kappa N^1$-bonding would be preferable if steric congestion around the metal center does not interfere with coordination of $MeCN_4^-$, and the $Cp^*Ir(Me_2dtc)$ fragment seems to be compact enough for $\kappa N^1$-coordination. The Ir—N($MeCN_4$) bond in **5**·$HN_4CMe$, Ir1—N1 2.084(4) Å, is slightly shorter than Ir2—N4 2.109(4) Å in the dinuclear bpy complex **2**, which is consistent with the above argument for the steric requirement of the smaller $Me_2dtc^-$ coligand. The Ir—S($Me_2dtc$) bond lengths are 2.385(1) and 2.388(1) Å, which are comparable to those in $[Cp^*Ir(Me_2dtc)(N_3)]$.[26] The bond angle, Ir1—N1—C5 132.2(4)°, is slightly larger than Ir1—N1—N2 120.5(4)°, but the discrepancy in these angles is not so large as that in the corresponding bond angles in complex **2** (vide infra).



(2)

The product resulting from reaction with a stoichiometric amount of $HN_4CMe$ was isolated as the $PF_6$ (**6**) or OTf salt (eq 3). The crystal structure of **6** has been determined by X-ray analysis as a dinuclear complex bridged by $MeCN_4^-$ via the $N^1$ and $N^4$ atoms: $[\{Cp^*Ir(Me_2dtc)\}_2(\mu\text{-}MeCN_4\text{-}\kappa N^1:\kappa N^4)]PF_6$ (Figure 4). In this complex cation, two $Me_2dtc^-$ ligands are nearly parallel and oriented to the same direction. It is notable that, in contrast to the unsymmetrical dinuclear structure of the bpy complex in **2**, the $Me_2dtc$ complex in **6** is symmetrical with a $\mu$-$\kappa N^1$:$\kappa N^4$-bridging $MeCN_4^-$. This is the first example in which tetrazolate ($RCN_4^-$) acts as a $\mu$-$\kappa N^1$:$\kappa N^4$-bridging ligand. The coligand of $Me_2dtc^-$ is



(3)

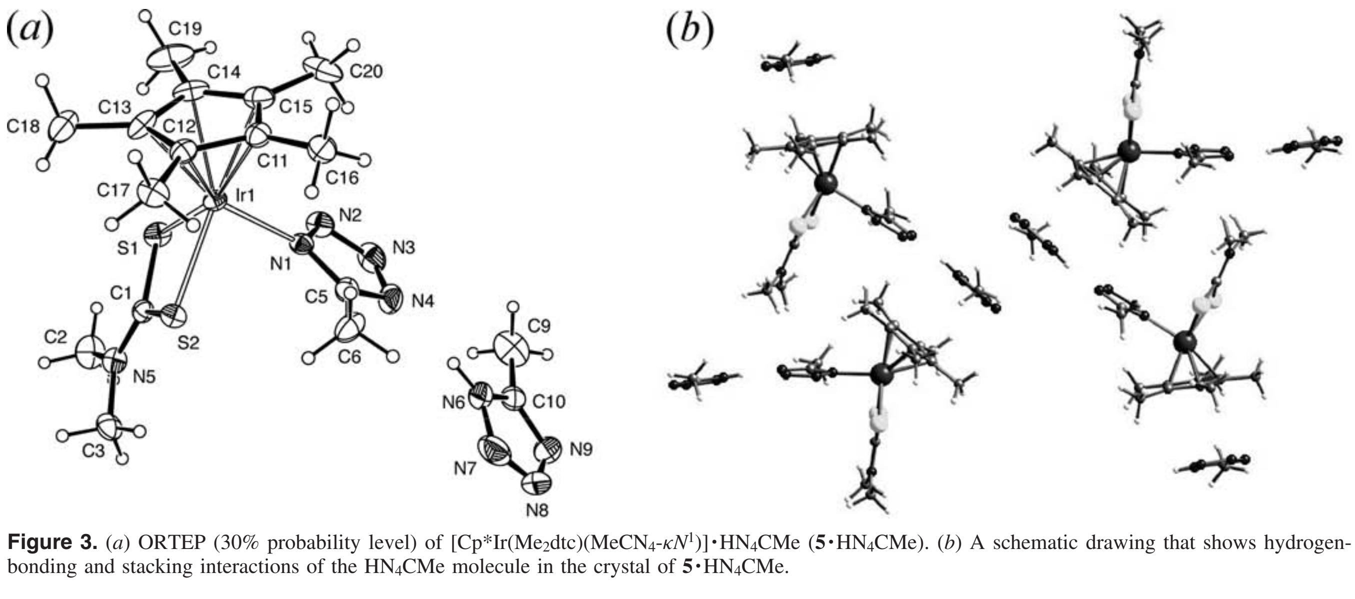


**Figure 3.** (*a*) ORTEP (30% probability level) of $[Cp^*Ir(Me_2dtc)(MeCN_4\text{-}\kappa N^1)]\cdot HN_4CMe$ (**5**·$HN_4CMe$). (*b*) A schematic drawing that shows hydrogen-bonding and stacking interactions of the $HN_4CMe$ molecule in the crystal of **5**·$HN_4CMe$.

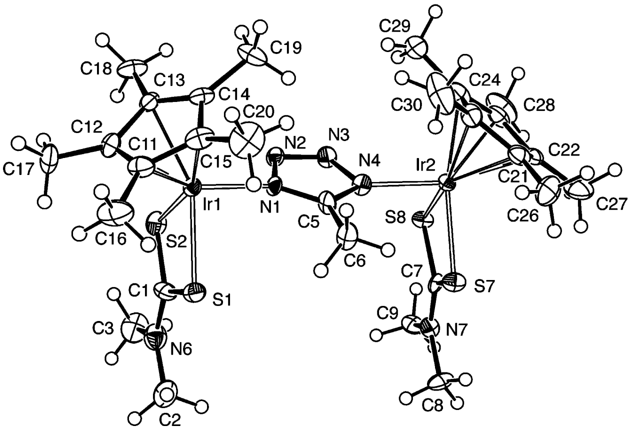
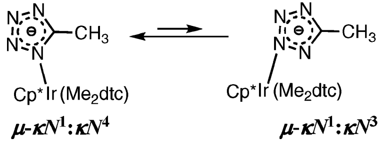


**Figure 4.** ORTEP (50% probability level) of the cation in $[\{\mathrm{Cp^*Ir(Me_2dtc)}\}_2(\mu\text{-}\mathrm{MeCN_4}\text{-}\kappa N^1{:}\kappa N^4)]\mathrm{PF_6}$ (**6**).

compact enough that steric interactions between two $\mathrm{Cp^*Ir(Me_2dtc)}$ fragments and between the complex fragment and the bridging $\mathrm{MeCN_4}^-$ group would be trivial, even if the $\mu\text{-}\kappa N^1{:}\kappa N^4$-bridging mode was assumed. Nevertheless, in the angular parameters of the bridging $\mathrm{MeCN_4}$ in **6**, there are relatively large discrepancies (ca. 20°) between Ir1—N1—C5 and Ir1—N1—N2 angles and between Ir2—N4—C5 and Ir2—N4—N3, as similarly observed at the $\kappa N^4$ bonding site of $\mathrm{MeCN_4}$ in **2**. The Ir—N($\mathrm{MeCN_4}$) bond lengths in **6**, Ir1—N1 2.097(6) and Ir2—N4 2.066(6) Å, and the Ir—S($\mathrm{Me_2dtc}$) bond lengths, 2.366(2)–2.399(2) Å, are comparable to those in the mononuclear complex **5**·$\mathrm{HN_4CMe}$.

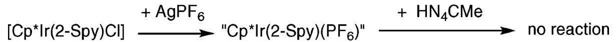
When crystals of **5**·$\mathrm{HN_4CMe}$ were dissolved in $\mathrm{CD_2Cl_2}$, the $^1$H NMR spectrum indicated that at least three species having a Cp* group exist in solution. The most abundant (ca. 60% at 30 °C) species showed the spectral pattern corresponding to the mononuclear structure of $[\mathrm{Cp^*Ir(Me_2dtc)(MeCN_4)}]$ (either the $\kappa N^1$-coordinated $\mathrm{MeCN_4}$ complex or its $\kappa N^2$-linkage isomer). On the other hand, the $^1$H NMR spectral pattern of **5**·$\mathrm{HN_4CMe}$ in $\mathrm{CD_3CN}$ (at 30 °C) was completely different, and the main signals (ca. 67%) were consistent with the $\mu\text{-}\kappa N^1{:}\kappa N^4$-bridging dinuclear structure, $[\{\mathrm{Cp^*Ir(Me_2dtc)}\}_2(\mu\text{-}\mathrm{MeCN_4}\text{-}\kappa N^1{:}\kappa N^4)]^+$ (the same cation in **6**). Furthermore, when crystals of dinuclear complex **6** were dissolved in $\mathrm{CD_3CN}$, the $^1$H NMR spectrum (at 30 °C) indicated the existence of an isomeric mixture of the $\mu\text{-}\kappa N^1{:}\kappa N^4$- and $\mu\text{-}\kappa N^1{:}\kappa N^3$-bridging species in the ratio of ca. 3:1 (eq 4). Thus, it is concluded that the $\mathrm{Me_2dtc}$ complexes afford a mixture of interconverting bonding modes in solution, whereas more strongly bound bpy and phen ligands give configurationally stable complexes.



(4)

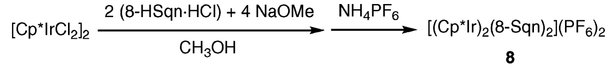
## Structures of 2-Pyridinethiolato and 8-Quinolinethiolato Complexes and Their Reactivity toward $\mathrm{MeCN_4}^-$.

As seen in the above sections, the ligand of $\mathrm{MeCN_4}^-$ bridged two $\mathrm{Cp^*Ir^{III}(L\text{–}L)}$ fragments in the $\mu\text{-}\kappa N^1{:}\kappa N^3$ and $\mu\text{-}\kappa N^1{:}\kappa N^4$ modes when the coligand (L—L) was bpy/phen and $\mathrm{Me_2dtc}^-$, respectively. Therefore, it is interesting to examine the synthesis and structure of the $\mathrm{MeCN_4}$-bridging complex with a hybrid-type pyridine—thiolate or quinoline—thiolate chelating ($\kappa^2 N,S$) ligand: 2-Spy or 8-Sqn. At first, using the 2-Spy precursor complex, a similar reaction to that for the dinuclear complex of **2**, **4**, or **6** was attempted. From a reaction mixture of [Cp*Ir(2-Spy)Cl] and $\mathrm{AgPF_6}$ in MeOH, the precipitated AgCl was filtered off, and the yellow filtrate was mixed with an equivalent molar quantity of $\mathrm{HN_4CMe}$. However, from this mixture, no product containing $\mathrm{MeCN_4}^-$ as a ligand could be obtained (eq 5). To see the reason why such a reaction with $\mathrm{HN_4CMe}$ was prohibited, the precursor complex of Cp*Ir(2-Spy)($\mathrm{PF_6}$) has been characterized. X-ray crystallography revealed that the complex, $[(\mathrm{Cp^*Ir})_2(\mu\text{-2-Spy-}\kappa^2 S,N{:}\kappa S)_2](\mathrm{PF_6})_2$ (**7**), has a dinuclear structure with two $\mu\text{-}\kappa^2 S,N{:}\kappa S$-bridging 2-Spy ligands (part *a* of Figure 5).



$$[\mathrm{Cp^*Ir(2\text{-}Spy)Cl}] \xrightarrow[-\,\mathrm{AgCl}]{+\,\mathrm{AgPF_6}} \text{“}\mathrm{Cp^*Ir(2\text{-}Spy)(PF_6)}\text{”}\ (\mathbf{7}) \xrightarrow[\mathrm{CH_3CN/CH_3OH}]{+\,\mathrm{HN_4CMe}} \text{no reaction} \qquad (5)$$

The corresponding 8-quinolinethiolato (8-Sqn) complex was prepared directly from a reaction of $[\mathrm{Cp^*IrCl_2}]_2$ and Na(8-Sqn) (without $\mathrm{Cl}^-$ extraction using $\mathrm{Ag}^+$ ion) and crystallized as the $\mathrm{PF_6}$ salt upon the addition of $\mathrm{NH_4PF_6}$ (eq 6). The X-ray analysis of the recrystallized product, $[(\mathrm{Cp^*Ir})_2(8\text{-}\mathrm{Sqn})_2](\mathrm{PF_6})_2\cdot{}^1/_2\mathrm{CH_3CN}$ (**8**·$^1/_2\mathrm{CH_3CN}$), confirmed a similar dinuclear structure with $\mu\text{-}\kappa^2 S,N{:}\kappa S$-bridging 8-Sqn ligands (part *b* of Figure 5). In both complexes of **7** and **8**, the two pyridyl or quinolyl groups in the bridging ligands take a syn configuration with respect to a nearly planar $\mathrm{Ir_2S_2}$ square; the dinuclear complex dication has pseudo-$C_2$ symmetry. This molecular structure should be favored, as compared to the pseudo-$C_i$ isomer with an anti configuration, by the intramolecular stacking interaction between two pyridyl or quinolyl rings. In the 2-Spy complex **7**, the dihedral angle between the pyridyl planes is 18.9(2)°, and the closest contact distances of N31···C42 and N41···C32 are 3.018(4) and 3.001(4) Å, respectively. In relation to this stacking interaction, the Ir—S bond lengths in the $\mathrm{Ir_2S_2}$ core show a characteristic feature, that is, the bridging bonds, Ir1—S2 2.4063(8) and Ir2—S1 2.4052(9) Å, are shorter than the bonds in the four-membered chelate rings, Ir1—S1 2.4454(9) and Ir2—S2 2.4514(9) Å. This would be the reason why the 2-Spy bridges in the dinuclear complex **7** are so stable and do not react with $\mathrm{HN_4CMe}$.



$$[\mathrm{Cp^*IrCl_2}]_2 \xrightarrow[\mathrm{CH_3OH}]{2\,(8\text{-}\mathrm{HSqn\cdot HCl}) + 4\,\mathrm{NaOMe}} \xrightarrow{\mathrm{NH_4PF_6}} [(\mathrm{Cp^*Ir})_2(8\text{-}\mathrm{Sqn})_2](\mathrm{PF_6})_2\ (\mathbf{8}) \qquad (6)$$

In the case of the 8-Sqn complex **8**·$^1/_2\mathrm{CH_3CN}$, the dihedral angle between the quinolyl planes is 12.10(9)° and the closest

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(26) Suzuki, T.; DiPasquale, A. G.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 10514–10515.

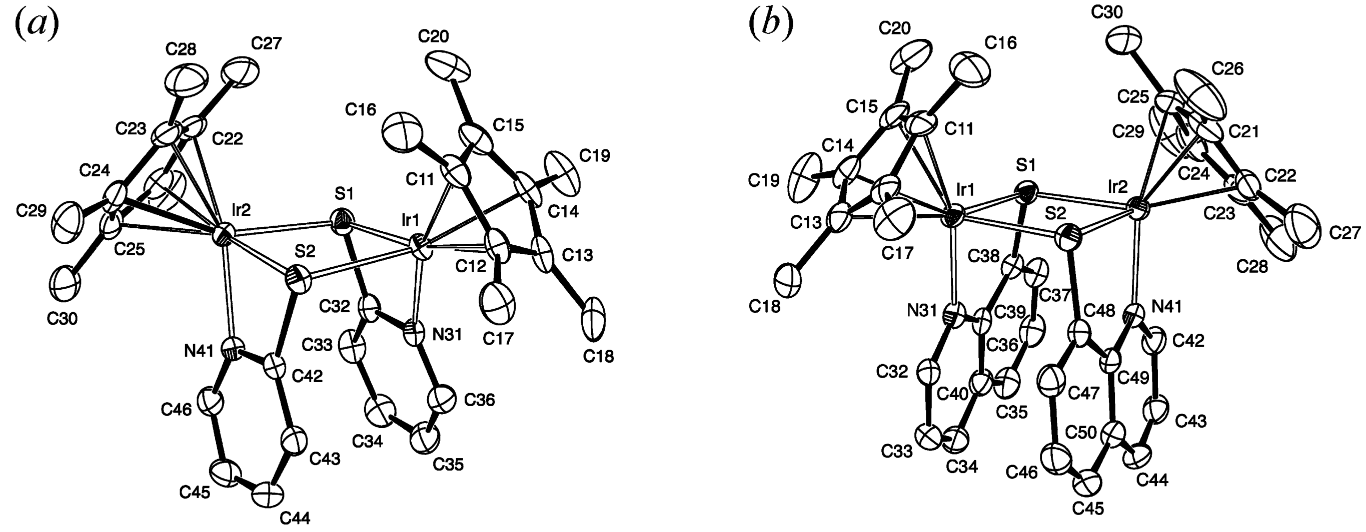
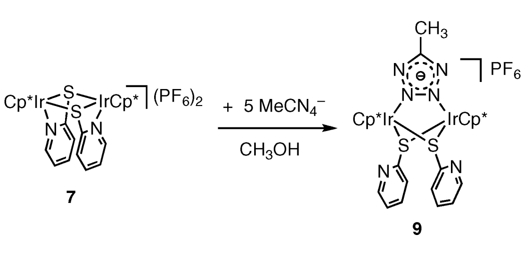


**Figure 5.** ORTEPs (50% probability level, hydrogen atoms omitted) of the dinuclear cationic complexes in (*a*) [(Cp*Ir)$_2$($\mu$-2-Spy-$\kappa^2S,N$:$\kappa S$)$_2$](PF$_6$)$_2$ (**7**) and (*b*) [(Cp*Ir)$_2$($\mu$-8-Sqn-$\kappa^2S,N$:$\kappa S$)$_2$](PF$_6$)$_2\cdot{}^1/_2$CH$_3$CN (**8**$\cdot{}^1/_2$CH$_3$CN).

contact distances of N31···C48 and N41···C38 are 3.023(4) and 3.059(4) Å, respectively. The bridging Ir—S bonds are Ir1—S2 2.4142(9) and Ir2—S1 2.4148(8) Å, which are comparable to those in the 2-Spy complex **7**. On the other hand, the Ir—S bonds in the five-membered 8-Sqn chelate rings, Ir1—S1 2.3652(8) and Ir2—S2 2.3655(8) Å, are markedly shorter than the Ir—S bonds in the four-membered 2-Spy chelate rings in **7**. The Ir—N(py) bond lengths in **7** are 2.088(3) and 2.098(3) Å, and the Ir—N(qn) lengths in **8** are 2.102(3) and 2.108(3) Å. It is, thus, suggested that the steric strain arising from the formation of the four-membered 2-Spy chelate ring in **7** did not alter the Ir—N(py) bond length and elongated the Ir—S bond in the chelate ring. This could be due to the higher angular flexibility of the thiolate (S$^-$) coordination than the pyridine (py) one.

The reaction of **7** with quintuple the molar quantity of Na(N$_4$CMe) gave a gradual color change to lighter yellow, and pale-yellow crystals of the product PF$_6$ salt (**9**) could be isolated (eq 7). The elemental analysis suggested the composition of the MeCN$_4$-bridged complex of (Cp*Ir)$_2$(2-Spy)$_2$(MeCN$_4$)(PF$_6$), as similar to complexes **2**, **4**, and **6**. The X-ray crystallographic analysis of **9**, however, determined the triply bridged dinuclear structure of the complex cation (Figure 6), with two $\mu$-$\kappa S$:$\kappa S$-bridging 2-Spy and a $\mu$-$\kappa N^2$:$\kappa N^3$-bridging MeCN$_4$ ligands. The nitrogen site of 2-Spy was uncoordinated in this complex, **9**. Interestingly, in the reaction with excess MeCN$_4^-$ the Ir—N(py) bonds of **7** were cleaved, whereas the elongated Ir—S bonds in the 2-Spy chelate rings maintained to form $\mu$-$\kappa S$:$\kappa S$-bridges. Similar dinuclear structures with bridging two thiolato (SR) ligands and a pyrazolato (pz) ligand have been reported in the Cp*Rh$^{III}$ complexes: [(Cp*Rh)$_2$($\mu$-pz)($\mu$-SR)$_2$]BF$_4$ (R = C$_6$H$_5$, *p*-C$_6$F$_4$H).[27]



(7)

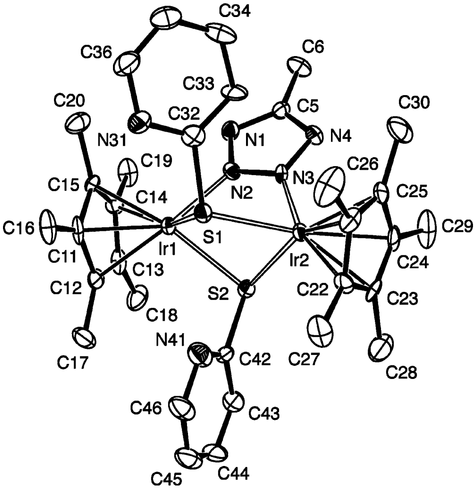


**Figure 6.** ORTEP (30% probability level, hydrogen atoms omitted) of the cation in [(Cp*Ir)$_2$($\mu$-2-Spy-$\kappa S$:$\kappa S$)$_2$($\mu$-MeCN$_4$-$\kappa N^2$:$\kappa N^3$)]PF$_6$ (**9**).

The Ir—S bond lengths in **9** are 2.377(3)–2.399(3) Å, which are similar in length to those in **7** and **8**, suggesting that the $\mu$-$\kappa S$:$\kappa S$-bridge in **9** is stable. The bridging mode of MeCN$_4^-$ is $\mu$-$\kappa N^2$:$\kappa N^3$; it is easily assumed that this mode is the most sterically preferable when the tetrazolate binds two metal centers in the (Cp*Ir)$_2$($\mu$-2-Spy-$\kappa S$:$\kappa S$)$_2$ fragment. The Ir—N(MeCN$_4$) bonds are Ir1—N2 2.079(8) and Ir2—N3 2.082(9) Å, which correspond well to the Ir—N(pz) bonds in related pyrazolate-[25] or 4-methylpyrazolate-bridged complexes.[28]

When crystals of **9** were dissolved in CD$_2$Cl$_2$ or CD$_3$CN, the $^1$H NMR spectrum of each solution showed the existence of a complicated mixture of more than six species having a coordinated MeCN$_4$. For a structurally similar dinuclear

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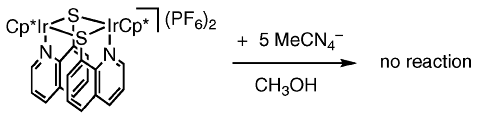
(27) García, J. J.; Barón, G.; Arévalo, A.; Torrens, H.; Carmona, D.; Esteban, M.; Lohoz, F. J.; López, J. A.; Oro, L. A. *J. Organomet. Chem.* **1998**, *551*, 55–65.

(28) Faure, M.; Onidi, A.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **2001**, *634*, 12–18.

Cp*Rh$^{III}$ complex, [(Cp*Rh)$_2$($\mu$-pz)($\mu$-SC$_6$H$_5$)$_2$]BF$_4$, a fluxional behavior is observed in solution, owing to the isomerization process among the syn-exo, anti, and syn-endo isomers dependent on the orientation of a pair of thiolate—phenyl groups.[27] In addition, for the present 2-Spy/MeCN$_4$ complex, it is possible that one of the pyridyl-N atoms recoordinates to an iridium center, affording an asymmetrical dinuclear complex bearing a monodentate (either $\kappa N^1$- or $\kappa N^2$-coordinated) MeCN$_4$ ligand at the other iridium atom: [Cp*Ir($\mu$-2-Spy-$\kappa^2 S,N$:$\kappa S$)($\mu$-2-Spy-$\kappa S$:$\kappa S$)(MeCN$_4$-$\kappa N$)IrCp*]$^+$. Another partially dissociated mono- and dinuclear complex containing MeCN$_4$ may possibly exist. Thus, it is concluded that the molecular structure of **9** with two $\mu$-$\kappa S$:$\kappa S$-bridging 2-Spy ligand and a $\mu$-$\kappa N^2$:$\kappa N^3$-bridging MeCN$_4$ ligand is not stable in solution. However, pale-yellow crystals of **9** were reprecipitated nearly quantitatively from the above solution by slow evaporation.

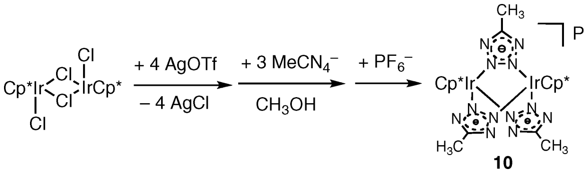
The 8-Sqn-bridged complex **8** was stable toward the addition of excess Na(N$_4$CMe) (eq 8); **8** was recovered quantitatively from the reaction mixture. This fact is consistent with the shorter Ir—S(bridge or chelate) bond lengths in **8**, as compared to the Ir—S(chelate) bonds in the 2-Spy complex of **7**.



**8**

(8)

**Triply $\mu$-MeCN$_4$-$\kappa N^2$:$\kappa N^3$-Bridged Complex.** As shown in the above sections, the bridging modes of MeCN$_4^-$ in dinuclear [(Cp*Ir$^{III}$)$_2$(L—L)$_2$(MeCN$_4$)]$^{n+}$ complexes are dependent on the kind of L—L coligands. Therefore, it is intriguing to investigate the structure of the MeCN$_4$-bridging complex without any coligand. The reaction of [Cp*IrCl$_2$]$_2$, AgOTf, and Na(N$_4$CMe) in the molar ratio of 1:4:3 afforded such a complex, and the product could be crystallized upon the addition of NH$_4$PF$_6$ as yellow needle crystals having the chemical formula of [(Cp*Ir)$_2$(MeCN$_4$)$_3$]PF$_6$·$^1/_2$CH$_3$CN (**10**·$^1/_2$CH$_3$CN) (eq 9). Repeated recrystallization of this compound from (wet) acetonitrile/diethyl ether gave a few pieces of yellow columnar crystals, which were probably a dihydrate of the desired complex PF$_6$ salt: [(Cp*Ir)$_2$(MeCN$_4$)$_3$]PF$_6$·2H$_2$O (**10**·2H$_2$O). X-ray crystallography revealed the triply bridging $\mu$-MeCN$_4$-$\kappa N^2$:$\kappa N^3$ structure of the dinuclear complex cation (Figure 7). Up to now, several crystal structures of dinuclear Cp*Ir$^{III}$ complexes bridged by one or two pyrazolate derivatives are reported,[25,28] but this is the first example of the triply bridged dinuclear Cp*Ir$^{(III)}$ complex, to our best knowledge. The two Cp* rings are nearly parallel to each other; the dihedral angle between them is only 1.5(6)°, and three MeCN$_4$ planes have dihedral angles of 119.0(4), 105.4(4), and 134.4(4)°. The Ir—N(N$_4$CMe) bond lengths are in the range of 2.088(9)–2.111(9) Å, and the Ir1···Ir2 distance is 3.923(4) Å.



(9)

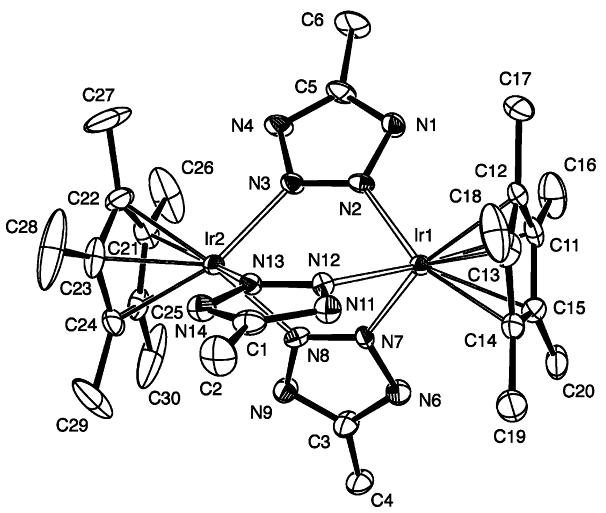


**Figure 7.** ORTEP (30% probability level, hydrogen atoms omitted) of the cation in [(Cp*Ir)$_2$($\mu$-MeCN$_4$-$\kappa N^2$:$\kappa N^3$)$_3$]PF$_6$·2H$_2$O (**10**·2H$_2$O).

**10** in CD$_3$CN exhibited a simple $^1$H NMR spectrum, consisting of one Cp* and one MeCN$_4$ resonance in the integration ratio of 5:3. This spectral feature is indicative of the stability of the triply bridged structure in solution.

## Concluding Remarks

For 5-methyltetrazolate (MeCN$_4^-$), two monodentate coordination modes and four bridging modes are possible (Scheme 1). In this study with Cp*Ir$^{III}$(L—L) fragments, mononuclear complexes with both $\kappa N^1$- and $\kappa N^2$-coordination modes and dinuclear complexes having three kinds of bridging modes (except for the $\mu$-$\kappa N^1$:$\kappa N^2$ one) have been synthesized selectively, depending on the coligands (L—L) and the reaction ratio of HN$_4$CMe or Na(N$_4$CMe) applied. All of the bonding modes have been confirmed by X-ray analyses. The Me$_2$dtc complex of [{Cp*Ir(Me$_2$dtc)}$_2$($\mu$-MeCN$_4$-$\kappa N^1$:$\kappa N^4$)]PF$_6$ (**6**) is the first dinuclear complex having the $\mu$-$\kappa N^1$:$\kappa N^4$-bridging mode of tetrazolates.

The most important factor for determining the bridging mode of MeCN$_4^-$ would be the steric requirement from the coligand, L—L. Because the bpy and phen ligands are planar and rather bulky, the $\mu$-$\kappa N^1$:$\kappa N^3$ bridge is the only sterically possible mode in [{Cp*Ir(bpy or phen)}$_2$(MeCN$_4$)]$^{3+}$, which gives a characteristic pyramidal pocket surrounded by two bpy/phen ligands and a MeCN$_4$ ligand. In contrast, in the case where the coligand is compact enough as that for Me$_2$dtc$^-$, the $\kappa N^1$-coordination mode of MeCN$_4^-$ is preferable because of the higher basicity of the $N^1$ site versus $N^2$.[18b] In fact, the $\kappa N^1$-coordination and the $\mu$-$\kappa N^1$:$\kappa N^4$-bridging modes were confirmed in the mononuclear and the dinuclear Me$_2$dtc complexes **5** and **6**, respectively. Both complexes, however, showed a complicated $^1$H NMR spectrum (in CD$_3$CN or CD$_2$Cl$_2$) due presumably to partial dissociation (and recoordination through the other bonding site) of MeCN$_4^-$ in solution. This may be related to the lower positive charge of the Cp*Ir($Me_2$dtc)$^+$ fragment, as compared to the Cp*Ir(bpy or phen)$^{2+}$ fragments.

The most striking feature in this study is the reduced reactivity of the 2-Spy and 8-Sqn complexes (**7** and **8**) toward the addition of $HN_4CMe$ (eqs 5 and 8), although the coligands can be considered as hybrids of bpy/phen and $Me_2dtc^-$. The crystal structures of **7** and **8** shed light on the factors contributing to this observation. Owing to the intramolecular stacking interaction between the pyridine or quinoline rings (Figure 5), the $\mu$-$\kappa S$:$\kappa S$ bridges in [(Cp*Ir)$_2$($\mu$-2-Spy or 8-Sqn-$\kappa^2S,N$:$\kappa S$)$_2$]$^{2+}$ are extremely stable. In **7**, the chelate ($\kappa^2S,N$) coordination of 2-Spy forming a four-membered ring suffered a large strain, as revealed in their bond angles, and the chelate ring could be cleaved by the reaction with excess Na($N_4CMe$). This reaction, however, maintained the $\mu$-$\kappa S$:$\kappa S$ bridges of two 2-Spy ligands, and $MeCN_4$ bound two Ir$^{III}$ centers of the (Cp*Ir)$_2$($\mu$-2-Spy-$\kappa S$:$\kappa S$)$_2$ fragment in the most sterically favorable way: $\mu$-$\kappa N^2$:$\kappa N^3$ (**9**).

In comparison with the structural parameters of the $MeCN_4$ moiety in the various kinds of $MeCN_4$ complexes described in this study, there were no apparent differences attributable to the coordination/bridging modes of $MeCN_4^-$. Therefore, the bonding mode of $MeCN_4$ does not alter the properties of the ligand itself, and it is concluded that steric demand of the metal fragment is the determining factor for the bonding mode of $MeCN_4^-$.

## Experimental Section

**Materials and Measurements.** The starting iridium(III) complexes [Cp*IrCl$_2$]$_2$,[29] [Cp*IrCl(bpy or phen)]Cl,[24a,30] [Cp*Ir($N_3$)(bpy)]$PF_6$,[23] [Cp*Ir($Me_2$dtc)Cl],[26] and [Cp*Ir(2-Spy)Cl][31] were synthesized according to literature methods. The phen complexes, [Cp*Ir(Cl or $N_3$)(phen)]$PF_6$, were prepared by similar methods to those of the bpy analogues. $^1$H NMR spectra were acquired on a Jeol EX-270 or 400 spectrometer at 30 °C; the chemical shifts were referenced to residual $^1$H NMR signals of solvents and are reported versus TMS.

**[Cp*Ir(bpy)($MeCN_4$-$\kappa N^2$)]$PF_6$ (1).** To a methanol solution (1 cm$^3$) of [Cp*IrCl(bpy)]Cl (10.6 mg, 0.019 mmol) was added a methanol solution (1 cm$^3$) of AgOTf (10.7 mg, 0.042 mmol) with stirring. The mixture was allowed to stand in the dark overnight, and the resulting white precipitate (AgCl) was filtered off and washed with a small amount (ca. 1 cm$^3$) of methanol. The filtrate and washings were combined and mixed with a methanol solution (2 cm$^3$) containing 5-methyltetrazole (7.6 mg, 0.090 mmol) and sodium methoxide (4.9 mg, 0.091 mmol). After stirring for ca. 30 min, the mixture was filtered off to remove a small amount of white precipitate, probably Ag($N_4CMe$), and a methanol solution (1 cm$^3$) of $NH_4PF_6$ (1.35 mg, 0.083 mmol) was added to the filtrate. Diffusion of diethyl ether vapor into the mixture in a closed vessel afforded yellow prismatic crystals, which were collected by filtration and dried in air. Yield: 6.7 mg (49%). Anal. Found: C, 37.03; H, 3.76; N, 11.80. Calcd for $C_{22}H_{26}F_6IrN_6P$: C, 37.13; H, 3.68; N, 11.81. $^1$H NMR ($CD_3CN$, 303 K): $\delta$ 1.60 (s, Cp*, 15H), 2.13 (s, $MeCN_4$, 3H), 7.81 (m, bpy, 2H), 8.21 (m, bpy, 2H), 8.36 (m, bpy, 2H), and 9.07 (m, bpy, 2H).

**[{Cp*Ir(bpy)}$_2$($\mu$-$MeCN_4$-$\kappa N^1$:$\kappa N^3$)](PF6)$_3$·2$H_2O$ (2·2$H_2O$).** To a methanol solution (2 cm$^3$) of [Cp*IrCl(bpy)]Cl (154 mg, 0.278 mmol) was added a methanol solution (1 cm$^3$) of AgOTf (138 mg, 0.537 mmol) with stirring. The mixture was stirred in the dark at room temperature overnight, and the white precipitate was filtered off. To the yellow filtrate was added a methanol solution (1 cm$^3$) of 5-methyltetrazole (24 mg, 0.29 mmol) with stirring. The mixture, after standing for ca. 30 min, was filtered to remove a small amount of white precipitate, and a methanol solution (2 cm$^3$) of $NH_4PF_6$ (217 mg, 1.33 mmol) was added with stirring. The yellow precipitate formed was collected by filtration, and the crude product was recrystallized from an acetonitrile solution by vapor diffusion of diethyl ether, depositing yellow block crystals of **2**. Yield: 121 mg (57%). Anal. Found: C, 33.43; H, 3.40; N, 7.49. Calcd for $C_{42}H_{53}F_{18}Ir_2N_8O_2P_3$: C, 33.16; H, 3.51; N, 7.37. $^1$H NMR ($CD_3CN$, 303 K): $\delta$ 1.31 (s, Cp*, 15H), 1.44 (s, Cp*, 15H), 1.85 (s, $MeCN_4$, 3H), and 7.85–8.88 (m, bpy, 16H).

**[{Cp*Ir(phen)}$_2$($\mu$-$MeCN_4$-$\kappa N^1$:$\kappa N^3$)]($PF_6$)$_3$ (4).** To a methanol solution (2 cm$^3$) of [Cp*IrCl(phen)]$PF_6$ (21.8 mg, 0.032 mmol) was added a methanol solution of AgOTf (8.8 mg, 0.034 mmol) with stirring. The mixture was allowed to stand in the dark overnight, and the white precipitate was removed by filtration. 5-Methyltetrazole (3.0 mg, 0.036 mmmol) in methanol (1 cm$^3$) was added with stirring to the filtrate, and the resulting white precipitate was filtered off. A methanol solution (1.5 cm$^3$) of $NH_4PF_6$ (16.5 mg, 0.10 mmol) was added, and the solvent was evaporated under ambient conditions. The residue was washed with methanol (1 cm$^3$) and recrystallized from acetonitrile by vapor diffusion of diethyl ether, affording yellow microcrystals. Yield: 14.0 mg (68%). Anal. Found: C, 36.79; H, 3.19; N, 7.11. Calcd for $C_{46}H_{49}F_{18}Ir_2N_8P_3$: C, 36.03; H, 3.22; N, 7.31. $^1$H NMR ($CD_3CN$, 303 K): $\delta$ 1.26 (s, Cp*, 15H), 1.46 (s, Cp*, 15H), 1.73 (s, $MeCN_4$, 3H), and 8.10–9.20 (m, phen, 16H).

**[Cp*Ir($Me_2$dtc)($MeCN_4$-$\kappa N^1$)]·$HN_4CMe$ (5·$HN_4CMe$).** To a methanol suspension (4 cm$^3$) of [Cp*Ir($Me_2$dtc)Cl] (48.2 mg, 0.100 mmol) was added a methanol solution (4 cm$^3$) of AgOTf (27.7 mg, 0.101 mmol) with stirring. The mixture was stirred in the dark at room temperature for 7 h. After removal of the white precipitate, a methanol solution (4 cm$^3$) containing $HN_4CMe$ (42.7 mg, 0.508 mmol) and NaOMe (27.7 mg, 0.513 mmol) was added to the filtrate, and the mixture was allowed to stand overnight. The white precipitate was filtered off, and the yellow filtrate was evaporated to dryness under reduced pressure. The residue was extracted with a minimum amount of methanol, and diethyl ether vapor was diffused into the filtrate, affording yellow crystals of **5**·$HN_4CMe$. When this compound was recrystallized repeatedly from methanol/diethyl ether, it was necessary to add a small amount of free $HN_4CMe$ to give fine crystals of the $HN_4CMe$ adduct, **5**·$HN_4CMe$. Yield: 23.4 mg (38%). Anal. Found: C, 33.23; H, 4.41; N, 20.41. Calcd for $C_{17}H_{28}IrN_9S_2$: C, 33.21; H, 4.59; N, 20.50. $^1$H NMR($CD_2Cl_2$, 303 K): main signals of **5** and $HN_4CMe$; $\delta$ 1.72 (s, Cp*, 15H), 2.47 (s, $N_4C$*Me*-$\kappa N^1$, 3H), 2.62 (s, *Me*$CN_4H$, 3H), and 3.04 (s, *Me*$_2$dtc, 6H).

**[{Cp*Ir($Me_2$dtc)}$_2$($\mu$-$MeCN_4$-$\kappa N^1$:$\kappa N^4$)]$PF_6$ (6).** [Cp*Ir($Me_2$dtc)Cl] (114 mg, 0.236 mmol) was dissolved in a mixture of methanol and acetonitrile (1:1, 5 cm$^3$), and a methanol solution (2 cm$^3$) of $AgPF_6$ (59.6 mg, 0.236 mmol) was added with stirring. The mixture was stirred in the dark for 2 h, and the resulting white precipitate was removed by filtration and washed with acetonitrile (2 cm$^3$) and methanol (2 cm$^3$). The filtrate and washings were combined and evaporated to dryness under reduced pressure. The

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**Table 1.** Crystallographic Data

| complex | **1** | **2**·2H$_2$O | **5** | **6** |
|---|---|---|---|---|
| formula | $C_{22}H_{26}F_6IrN_6P$ | $C_{42}H_{53}F_{18}Ir_2N_8O_2P_3$ | $C_{17}H_{28}IrN_9S_2$ | $C_{28}H_{45}F_6Ir_2N_0PS_4$ |
| fw | 711.66 | 1521.23 | 614.80 | 1123.31 |
| $T$ (K) | 200(2) | 200(2) | 200(2) | 200(2) |
| cryst color/habit | yellow/prism | yellow/block | yellow/plate | yellow/prism |
| cryst size (mm$^3$) | 0.25 × 0.15 × 0.15 | 0.24 × 0.14 × 0.10 | 0.30 × 0.10 × 0.10 | 0.20 × 0.10 × 0.10 |
| cryst syst | monoclinic | monoclinic | monoclinic | triclinic |
| space group, $Z$ | $P2_1/n$, 4 | $P2_1/n$, 4 | $P2_1/n$, 4 | $P\bar{1}$, 2 |
| $a$ (Å) | 8.8503(7) | 12.9780(10) | 9.0705(6) | 9.0077(10) |
| $b$ (Å) | 28.408(2) | 21.3291(14) | 23.6980(15) | 14.7648(14) |
| $c$ (Å) | 9.8675(5) | 20.4997(14) | 10.9302(6) | 15.3777(14) |
| α (deg) | 90 | 90 | 90 | 67.675(2) |
| $\beta$ (deg) | 93.760(2) | 109.086(2) | 92.542(2) | 76.876(2) |
| $\gamma$ (deg) | 90 | 90 | 90 | 87.743(2) |
| $V$ (Å$^3$) | 2475.6(3) | 5362.6(6) | 2382.8(6) | 1840.0(3) |
| $D_{calcd}$ (mg m$^{-3}$) | 1.909 | 1.884 | 1.740 | 2.028 |
| $F$(000) | 1384 | 2952 | 1208 | 1084 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 5.527 | 5.154 | 5.889 | 7.556 |
| $R_{int}$ | 0.032 | 0.037 | 0.037 | 0.041 |
| $T_{min}$, $T_{max}$ | 0.339, 0.491 | 0.371, 0.627 | 0.271, 0.591 | 0.313, 0.519 |
| reflns/params ratio | 5564/332 | 0.031 | 5288/272 | 8347/439 |
| R1 [$F_o^2 > 2\sigma(F_o^2)$] | 0.030 | 0.083 | 0.028 | 0.035 |
| wR2 (all reflns) | 0.072 | 1.039 | 0.081 | 0.171 |
| GOF | 1.194 | 1.039 | 1.244 | 1.056 |

| complex | **7** | **8**·$^1/_2$CH$_3$CN | **9** | **10**·2H$_2$O |
|---|---|---|---|---|
| formula | $C_{30}H_{38}F_{12}Ir_2N_2P_2S_2$ | $C_{39}H_{43.5}F_{12}Ir_2N_{2.5}P_2S_2$ | $C_{32}H_{41}F_6Ir_2N_6PS_2$ | $C_{26}H_{43}F_6Ir_2N_{12}O_2P$ |
| fw | 1165.08 | 1285.72 | 1103.20 | 1085.09 |
| $T$ (K) | 200(2) | 200(2) | 200(2) | 200(2) |
| cryst color/habit | yellow orange/block | orange/block | yellow/block | yellow/prism |
| cryst size (mm$^3$) | 0.25 × 0.15 × 0.12 | 0.20 × 0.15 × 0.11 | 0.12 × 0.12 × 0.10 | 0.20 × 0.15 × 0.15 |
| cryst syst | triclinic | monoclinic | triclinic | triclinic |
| space group, $Z$ | $P\bar{1}$, 2 | $P2_1/a$, 4 | $P\bar{1}$, 2 | $P\bar{1}$, 2 |
| $a$ (Å) | 11.2017(7) | 14.2968(4) | 11.1094(11) | 11.5401(10) |
| $b$ (Å) | 13.8270(8) | 12.9142(4) | 11.9138(11) | 11.7447(12) |
| $c$ (Å) | 14.2626(7) | 23.2092(7) | 14.9292(15) | 14.9334(16) |
| α (deg) | 92.211(2) | 90 | 84.212(3) | 87.023(2) |
| $\beta$ (deg) | 112.059(2) | 100.989(1) | 72.713(2) | 67.242(2) |
| $\gamma$ (deg) | 112.396(2) | 90 | 81.066(3) | 83.122(3) |
| $V$ (Å$^3$) | 1849.90(18) | 4206.6(2) | 1860.7(3) | 1853.0(3) |
| $D_{calcd}$ (Mg m$^{-3}$) | 2.092 | 2,030 | 1.969 | 1.945 |
| $F$(000) | 1112 | 2476 | 1060 | 1044 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 7.472 | 6.583 | 7.362 | 7.290 |
| $R_{int}$ | 0.022 | 0.035 | 0.036 | 0.035 |
| $T_{min}$, $T_{max}$ | 0.257, 0.467 | 0.353, 0.506 | 0.472, 0.526 | 0.323, 0.408 |
| reflns/params ratio | 8438/462 | 9574/552 | 8516/454 | 8310/442 |
| R1 [$F_o^2 > 2\sigma(F_o^2)$] | 0.022 | 0.024 | 0.042 | 0.057 |
| wR2 (all reflns) | 0.067 | 0.050 | 0.129 | 0.154 |
| GOF | 1.164 | 1.018 | 1.235 | 1.190 |

orange residue was extracted with acetonitrile (2 cm$^3$), and 5-methyltetrazole (20.0 mg, 0.238 mmol) was added to the filtered extract. Addition of a few drops of methanol, followed by vapor diffusion of diethyl ether into the mixture, deposited yellow prismatic crystals, which were collected by filtration and air-dried. Yield: 109 mg (82%). Anal. Found: C, 30.11; H, 3.98; N, 7.61. Calcd for $C_{28}H_{45}F_6Ir_2N_6PS_4$: C, 29.94; H, 4.04; N, 7.48. $^1$H NMR (CD$_3$CN, 303 K): main signals of **6**; $\delta$ 1.68 (s, Cp*, 30H), 2.50 (s, MeCN$_4$, 3H), and 3.02 (s, Me$_2$dtc, 6H); minor signals of the linkage isomer (**6′**); $\delta$ 1.67 (s, Cp*, 5H), 1.73 (s, Cp*, 5H), 2.41 (s, MeCN$_4$, 1H), 3.01 (s, Me$_2$dtc, 2H), and 3.07 (s, Me$_2$dtc, 2H). The corresponding OTf salt, [{Cp*Ir(Me$_2$dtc)}$_2$($\mu$-MeCN$_4$-$\kappa N^1$:$\kappa N^4$)]OTf, was similarly prepared using AgOTf, instead of AgPF$_6$. Yield: 52%. Anal. Found: C, 30.96; H, 4.01; N, 7.50. Calcd for $C_{29}H_{45}F_3Ir_2N_6O_3S_5$: C, 30.89; H, 4.02; N, 7.45.

**[(Cp*Ir)$_2$($\mu$-2-Spy-$\kappa S,N$:$\kappa S$)$_2$](PF$_6$)$_2$ (7).** A methanol solution (2 cm$^3$) of AgPF$_6$ (27 mg, 0.105 mmol) was added with stirring to a methanol solution (3 cm$^3$) of [Cp*Ir(2-Spy)Cl] (50 mg, 0.105 mmol). The resulting white precipitate was filtered off and washed twice with methanol (2 cm$^3$). The filtrate and washings were combined and evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane, and the filtered extract was concentrated to a small volume under reduced pressure. Diffusion of diethyl ether vapor into the concentrate gave yellow-orange crystals, which were collected by filtration and dried in air. Yield: 40 mg (64%). Anal. Found: C, 31.13; H, 3.32; N, 2.46. Calcd for $C_{30}H_{38}F_{12}Ir_2N_2P_2S_2$: C, 30.93; H, 3.29; N, 2.40. $^1$H NMR (CD$_3$CN, 303 K): $\delta$ 1.76 (s, Cp*, 15H), 6.73 (ddd, $J$ = 7.8, 1.2, 0.8 Hz, py-3H, 1H), 7.25 (ddd, $J$ = 7.8, 5.6, 1.2 Hz, py-5H, 1H), 7.68 (td, $J$ = 7.8, 1.6 Hz, py-4H, 1H), and 7.93 (ddd, $J$ = 5.6, 1.6, 0.8 Hz, py-6H, 1H).

**[(Cp*Ir)$_2$($\mu$-8-Sqn-$\kappa S,N$:$\kappa S$)$_2$](PF$_6$)$_2$·$^1/_2$CH$_3$CN (8·$^1/_2$CH$_3$CN).** To a suspension of [Cp*IrCl$_2$]$_2$ (358 mg, 0.450 mmol) in methanol (10 cm$^3$) was added a methanol solution (12 cm$^3$) containing 8-mercaptoquinoline hydrochloride (178 mg, 0.900 mmol) and NaOMe (97.6 mmol, 1.80 mmol) with stirring. The mixture was stirred for a few minutes, and undissolved materials were filtered off. The filtrate was evaporated to dryness, and the residue was extracted with a mixture of dichloromethane and acetonitrile (2:1, 10 cm$^3$). The filtered extract was evaporated, again, to dryness under reduced pressure, and the residue was dissolved in methanol. Addition of a large excess amount of a methanol solution of $NH_4PF_6$ gave a yellow-orange precipitate. The crude product was collected by filtration and recrystallized from acetonitrile by vapor diffusion of diethyl ether. Yield: 458 mg (79%). Anal. Found: C, 36.44; H, 3.37; N, 2.93. Calcd for $C_{39}H_{43.5}F_{12}Ir_2N_{2.5}P_2S_2$: C, 36.43; H, 3.41; N, 2.72. $^1$H NMR ($CD_3CN$, 303 K): $\delta$ 1.63 (s, Cp*, 15H), 6.92 (dd, $J = 8.4$, 5.4 Hz, qn-6H, 1H), 7.51 (dd, $J = 8.4$, 1.3 Hz, qn-7H, 1H), 7.60 (dd, $J = 8.5$, 7.0 Hz, qn-3H, 1H), 7.66 (dd, $J = 5.4$, 1.3 Hz, qn-5H, 1H), 7.83 (dd, $J = 7.0$, 1.2 Hz, qn-4H, 1H), and 8.00 (dd, $J = 8.5$, 1.2 Hz, qn-2H, 1H).

**[(Cp*Ir)$_2$($\mu$-2-Spy-$\kappa S$:$\kappa S$)$_2$($\mu$-MeCN$_4$-$\kappa N^2$:$\kappa N^3$)]PF$_6$ (9).** To a solution of **7** (63.6 mg, 0.054 mmol) in a mixture of methanol and acetonitrile (1:1, 2 cm$^3$) was added a methanol solution (2 cm$^3$) of 5-methyltetrazole (49.1 mg, 0.58 mmol) and NaOMe (31.4 mg, 0.58 mmol). The mixture was stirred at ambient temperature overnight and then evaporated to dryness by flow of a dry nitrogen stream. The residue was extracted with dichloromethane (5 cm$^3$), and the filtered extract was evaporated, again, to dryness. The residue was dissolved in a mixture of dichloromethane and methanol (1:1, 5 cm$^3$). Slow evaporation of the solution gave pale-yellow crystals of **9**. Yield: 40.2 mg (67%). Anal. Found: C, 34.76; H, 3.66; N, 7.73. Calcd for $C_{32}H_{41}F_6Ir_2N_6PS_2$: C, 34.84; H, 3.75; N, 7.62.

**[(Cp*Ir)$_2$($\mu$-MeCN$_4$-$\kappa N^2$:$\kappa N^3$)$_3$]PF$_6$·$^1/_2$CH$_3$CN (10·$^1/_2$CH$_3$CN).** To a methanol suspension (3 cm$^3$) of [Cp*IrCl$_2$]$_2$ (103 mg, 0.129 mmol) was added a methanol solution (3 cm$^3$) of AgOTf (131 mg, 0.511 mmol) with vigorous stirring. The mixture was allowed to stand in the dark for ca. 30 min, and the resulting white precipitate was filtered off. A mixture of 5-methyltetrazole (34.8 mg, 0.414 mmol) and sodium methoxide (23.4 mg, 0.433 mmol) in methanol (2 cm$^3$) was added to the orange filtrate; the color of the mixture turned immediately to yellow. After stirring at ambient temperature for 1 h, the white precipitate was filtered off, and a methanol solution (2 cm$^3$) of $NH_4PF_6$ (117 mg, 0.715 mmol) was added to the yellow filtrate. Standing the mixture for ca. 1 h precipitated yellow product, which was collected by filtration, washed with methanol, and dried in vacuo. The crude product was recrystallized from acetonitrile and gave yellow needle crystals of **10**·$^1/_2$CH$_3$CN. Yield: 63.6 mg (45%). Anal. Found: C, 30.18; H, 3.80; N, 16.43. Calcd for $C_{27}H_{40.5}F_6Ir_2N_{12.5}P$: C, 30.32; H, 3.82; N, 16.37. $^1$H NMR ($CD_3CN$, 303 K): $\delta$ 1.75 (s, Cp*, 30H) and 2.48 (s, MeCN$_4$, 9H).

**Crystallography.** The X-ray diffraction data were obtained at $-73(2)$ °C on a Rigaku R-axis rapid imaging plate detector with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å). A suitable crystal of each complex was mounted with a cryoloop and flash-cooled by a cold nitrogen stream. Data were processed by the *Process-Auto* program package,[32] and absorption corrections were applied either by the empirical method or by the numerical integration method.[33] The structures were solved either by the direct method using *SIR92*[34] or by a heavy-atom method using *DIRDIF99-PATTY*[35] and refined on $F^2$ (with all of the independent reflections) using the *SHELXL97* program.[36] For **1**–**9**, all of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms in the complexes were introduced at the positions calculated theoretically and treated with riding models. The hydrogen atoms of the solvents of crystallization (in **2**·H$_2$O and **8**·$^1/_2$CH$_3$CN) were not included in the calculation.

For **10**, repeated recrystallization from acetonitrile by vapor diffusion of diethyl ether deposited a few pieces of yellow columnar crystals suitable for X-ray diffraction study. The structural analysis revealed unambiguously the triply MeCN$_4$-bridged dinuclear structure of the complex cation, [(Cp*Ir)$_3$($\mu$-MeCN$_4$-$\kappa N^2$:$\kappa N^3$)$_3$]$^+$, but the positions of the fluorine atoms of the $PF_6^-$ anion were severely disordered. Furthermore, rather large electron densities remained at four separated positions, which were assumed to be disordered oxygen atoms of two water molecules. The disordered fluorine and oxygen atoms were refined with isotropic thermal parameters.

In the analysis of **9**, it could not be determined which of the ortho-positioned atoms are the (uncoordinated) nitrogen atoms of the $\mu$-$\kappa S$:$\kappa S$ bridging 2-Spy ligands. Therefore, in the reported structure we have assumed that one of the atoms is nitrogen and the other is C(—H) without any reliable reason. However, the other choice of N/C(—H) atoms did not alter the final results from the reported ones.

All of the calculations were carried out using the *CrystalStructure* software package.[37] Crystal data are collected in Table 1.

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**Supporting Information Available:** X-ray crystallographic information for all of the compounds analyzed in this study (PDF/CIF format), including the colored ORTEPs and tables of selected bond lengths and angles of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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